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DIFFERENCES OF POTENTIAL BETWEEN CADMIUM AND ALCOHOLIC SOLUTIONS OF SOME OF ITS SALTS

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In 1899 Kahlenberg[1] published an account of some experiments on the differences of potential established when metals are immersed in nonaqueous solutions of their salts. In this investigation he studied the behavior of silver, zinc, magnesium, cadmium, thallium, lead, copper, antimony, bismuth and iron in solutions of salts of these metals in nearly thirty organic solvents.

Previous to this work of Kahlenberg, Jones[2] had shown that the solution pressure of silver immersed in a solution of silver nitrate in ethyl alcohol is only about one-twentieth of the solution pressure of silver in an aqueous solution of the same salt. He also measured the potential differences between silver and solutions of silver nitrate in methyl alcohol and acetone. The highest electromotive force measured in acetone was 0.182 volt, while in methyl alcohol and ethyl alcohol the maximum values were 0.123 and 0.130 volt, respectively. Jones concludes from these experiments that

[1] Kahlenberg: J. Phys. Chem., 3, 379 (1899).
[2] Jones: Z. physik. Chem., 14, 346 (1894).

the solution pressure of the metal varies from one solvent to another. Later, Jones and Smith[1] studied the system

$$Zn—0.1\ N\ ZnCl_2\ in\ C_2H_5OH—0.1\ N\ ZnCl_2\ in\ H_2O—Zn$$

and concluded that the solution pressure of zinc in ethyl alcohol is 10^{-8} times its solution pressure in water. In 1893 Campetti[2] made some measurements of the potential differences between cadmium and nonaqueous solutions of its salts.

In all of the investigations cited no attempt was made to determine the change in electromotive force with the concentration of the electrolyte.

It has seemed of interest to study the cadmium electrode rather more closely than has been done hitherto and to determine, if possible, the solution pressure of this metal in several nonaqueous solvents.

Method of Experimentation

The differences of potential were measured by means of the familiar compensation method of Poggendorf, using as a zero instrument a Lippmann electrometer of improved form in which the mercury and sulphuric acid are permanently enclosed. With this instrument it was possible to make measurements correct to one millivolt except where the poor conductivity of the solutions or other disturbing factors rendered the readings less trustworthy. A chloride accumulator was used as the source of potential against which the experimental cell was balanced. The electromotive force of this cell was determined before and after each series of measurements by means of a Weston standard element, the electromotive force of which was 1.0197 volt at 20°, this voltage being based on the assumption that the electromotive force of a Clark cell at 15° is 1.434 volts.

One half of the experimental cell consisted of a normal calomel electrode prepared according to the directions given in Ostwald-Luther's Physiko-Chemische Messungen (p. 381)

[1] Jones and Smith: THIS JOURNAL, **23**, 397 (1900).
[2] Campetti: Atti accad. Torino, **29**, 61 and 228 (1893).

and was assumed to have an electromotive force of 0.56 volt, the positive sign indicating that the electrode was positive to the solution. The cadmium electrode and containing vessel composed the other half of the experimental cell.

The cadmium electrode was a rod of pure cadmium obtained from Kahlbaum, a copper wire being soldered to the top of the electrode in order to establish connection with the circuit. The cadmium and calomel electrodes were connected through an intermediate vessel containing some of the solution to be studied. The experimental cell was suspended by means of adjustable supports within a bath of water, the temperature of which was maintained at 20° with a possible variation of $\pm 0°.2$. At this temperature the electromotive force of the calomel electrode is 0.5612, the temperature coefficient being 0.0006 volt per degree.

The methyl and ethyl alcohols used were obtained from Kahlbaum and were subjected to treatment with lime for several weeks before they were required, when they were distilled into dry receivers which could be tightly stoppered. Merck's cadmium iodide and Kahlbaum's anhydrous cadmium chloride were the solutes employed, each being kept in a dry atmosphere for several days before making up the solutions.

The solutions were prepared by direct weighing of the solute and then making the solution up to a volume of 50 cc. in a calibrated measuring flask. In several cases the dilute solutions were prepared by dilution of the more concentrated solutions.

The general arrangement of the voltaic combination was as follows:

Cd—sol. Cd salt—sol. Cd salt—N KCl—HgCl—Hg

After each series of measurements on a solution of one concentration the experimental cell was taken apart and the cadmium electrode washed and then rubbed with a fresh piece of emery cloth to insure removal of any oxide or other substance which might interfere with the contact between metal

and solution. The electrode vessel and connecting vessel were thoroughly washed and dried, while the capillary tube connecting the calomel electrode with the other half of the experimental cell was washed and fresh N KCl forced through the tube.

The electromotive force developed at the junction of the two solutions, being very small, was disregarded in all of the calculations.

Results

The results of the measurements are given in Tables I to V, in which m denotes the molar concentration of the solution and π the electromotive force in millivolts, the prefixed sign indicating the potential of the cadmium electrode with reference to the solution. The data recorded in the tables are represented graphically in Fig. I.

The potentials given are the mean of a series of observations and in several cases represent the average of two entirely independent series made upon solutions of the same concentration.

It will be observed that the potential of the cadmium electrode in alcoholic solution becomes more strongly negative as the concentration increases.

In the case of the potential differences measured in solutions of cadmium iodide in methyl alcohol we are at a loss to account for the irregularities observed, especially with solutions of 0.08 and 0.10 molar concentration. When cadmium is immersed in solutions of cadmium iodide in ethyl alcohol of concentration less than 0.06 molar there is a reversal of polarity of the system and the current flows outside of the cell from cadmium to mercury instead of from mercury to cadmium, as in methyl alcohol and aqueous solutions. The curves *C* and *D* show the change in potential of the cadmium electrode when immersed in aqueous solutions of cadmium iodide and cadmium chloride, respectively.

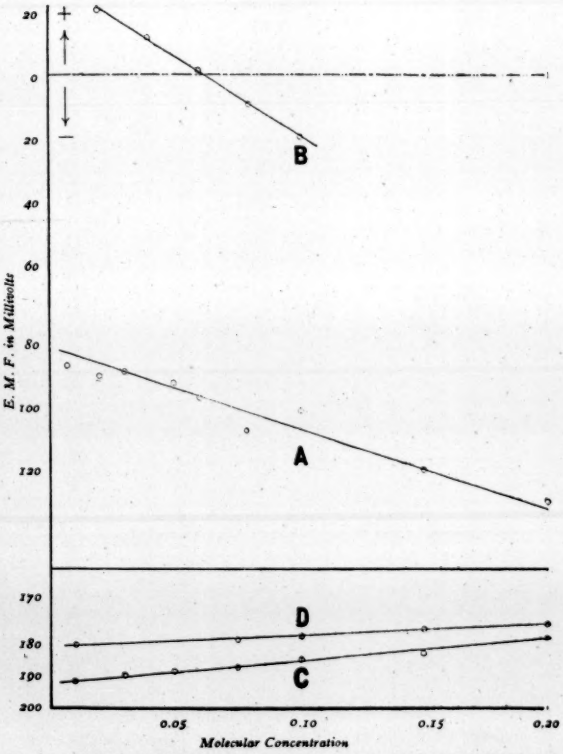

Fig. 1.—A. Cadmium iodide in methyl alcohol. B. Cadmium iodide in ethyl alcohol. C. Cadmium iodide in water. D. Cadmium chloride in water.

Table I—Cadmium Iodide in Methyl Alcohol

Temperature	m	ε
20°.0	0.01	— 82.6
19°.9	0.02	— 85.6
19°.9	0.03	— 84.2
20°.2	0.05	— 87.3
20°.0	0.06	— 91.7
20°.0	0.08	—101.0
20°.1	0.10	— 95.0
19°.9	0.15	—111.9
20°.1	0.20	—121.0

Table II—Cadmium Iodide in Ethyl Alcohol

Temperature	m	ε
20°.0	0.02	+18.6
19°.9	0.04	+10.5
19°.8	0.06	+ 1.0
20°.0	0.08	— 8.3
20°.0	0.10	—17.8

Table III—Cadmium Chloride in Methyl Alcohol

Temperature	m	ε
19°.9	sat. sol.	—113.0
20°.1	sat. sol.	—115.6
	Mean	—114.3

Table IV—Cadmium Iodide in Water

Temperature	m	ε
20°.2	0.01	—192.3
19°.8	0.03	—190.7
20°.2	0.05	—190.2
20°.0	0.075	—188.2
19°.8	0.10	—186.1
20°.0	0.15	—184.2
20°.2	0.20	—180.1

Table V—Cadmium Chloride in Water

Temperature	m	ε
20°.0	0.01	—182.0
19°.9	0.075	—180.5
20°.0	0.10	—179.4
19°.9	0.15	—177.4
19°.9	0.20	—176.0

It will be observed that in aqueous solution the potential of the cadmium electrode becomes less strongly negative as the concentration increases, or in other words, its behavior is exactly opposite to that in the alcohols. It is of interest to note that the slope of the curve *A* is approximately the mean of the slopes of the curves *B* and *C*, which is what we should expect from other investigations on the physical properties of methyl alcohol in comparison with the same properties of water and ethyl alcohol.

The potentials of the cadmium electrode in aqueous solutions of cadmium chloride have been studied by Labendzinski.[1] For the combination

$$\overset{-}{\mathrm{Cd}}\text{—}0.2\ \mathrm{N}\ \mathrm{CdCl_2}\text{—}0.2\ \mathrm{N}\ \mathrm{CdCl_2}\text{ — N KCl—HgCl—}\overset{+}{\mathrm{Hg}}$$

he finds an electromotive force of 0.738 volt, while for the same combination we find 0.737 volt.

Owing to its slight solubility in both methyl and ethyl alcohols, only two series of measurements were made on cadmium chloride in methyl alcohol. In a paper on the solubility of some inorganic salts in organic solvents Lobry de Bruyn[2] gives the following solubilities of cadmium chloride at 15°.5:

100 grams absolute methyl alcohol dissolve 1.71 grams cadmium chloride;

100 grams absolute ethyl alcohol dissolve 1.52 grams cadmium chloride.

In selecting cadmium chloride for this investigation it was assumed that these figures referred to the anhydrous salt, but it would appear that they must have been obtained with the hydrated salt, $\mathrm{CdCl_2.2H_2O}$. The measurements on cadmium chloride in methyl alcohol were confined to the saturated solution.

Discussion of Results

The electromotive force of the experimental cell is given by the equation

$$E = \pi + 0.5612$$

[1] Labendzinski: Z. Elek. Chem., **10**, 77 (1904).
[2] Lobry de Bruyn: Z. physik. Chem., **10**, 783 (1892).

or the potential of the cadmium electrode, referred to the solution, is

$$\pi = E - 0.5612$$

Applying Nernst's theory of the voltaic element we have as an expression for the osmotic work in transferring ions from the pressure P to the pressure p,

$$\int_p^P RT \frac{dp}{p} = RT \int_p^P \frac{dp}{p}$$

which on integration gives

$$RT \log_e \frac{P}{p}$$

The corresponding electrical work is $n\pi F$ where n is the valence of the ions and F is the quantity of electricity carried by 1 gram-equivalent of ions or 1 Faraday = 96580 coulombs. Equating electrical and osmotic work we have

$$n\pi F = RT \log_e \frac{P}{p}$$

or

$$\pi = \frac{RT}{nF} \log_e \frac{P}{p} \qquad (1)$$

Since osmotic pressure is proportional to the concentration we may substitute the ionic concentration, c, for p in equation (1), when we have

$$\pi = \frac{RT}{nF} \log_e \frac{P}{c} \qquad (2)$$

Except in the case of completely ionized electrolytes, c must be replaced by $m\alpha$ where m is the molar concentration of the solution and α is the degree of ionization. Assuming that the solution pressure remains constant for any one solvent, we may obtain from (2) an equation expressing the relation between the electrode potentials for two different ionic concentrations, c_1 and c_2. Letting π_1 and π_2 denote the elec-

trode potentials corresponding to ionic concentrations c_1 and c_2, we have

$$\pi_2 = \pi_1 + \frac{RT}{nF} \log_e \frac{c_2}{c_1} \qquad (3)$$

Inspection of (3) shows that if the electrode potential is positive it will be diminished by dilution, whereas if it is negative it will increase with dilution. In aqueous solutions of cadmium iodide and cadmium chloride the potential of the electrode increases (becomes more strongly negative) with dilution and consequently the electrode should be negative with reference to the solution. In alcoholic solutions the electrode potential diminishes (becomes more strongly positive) with dilution and therefore the electrode should be positive with reference to the solution. The experiments show that the cadmium electrode is negative in aqueous solutions, the potential difference increasing with dilution, whereas the cadmium electrode in alcoholic solution is negative, the potential difference decreasing with decrease in concentration and eventually reversing to a positive potential in the dilute solutions. The cadmium electrode can acquire a positive potential only when the combined electromotive force of the system is less than 0.5612 volt. The behavior of the cadmium electrode in alcoholic solution might be explained by assuming that the value of the term $\frac{RT}{nF} \log_e \frac{c_2}{c_1}$ in equation (3) is positive and increases with dilution. In the more concentrated solutions the value of this term would be positive but numerically less than π_1, which is negative, and therefore the value of π_2 would be negative also; as the concentration diminishes, the value of $\frac{RT}{nF} \log_e \frac{c_2}{c_1}$ would increase and eventually would become greater than π_1 when the value of π_2 would be positive. In order that the numerical value of $\frac{RT}{nF} \log_e \frac{c_2}{c_1}$ may increase we must assume $c_2 > c_1$ or $m_2\alpha_2 > m_1\alpha_1$.

A consequence of this assumption is that the degree of ionization must increase with dilution more rapidly than the dilution increases. This assumption is highly improbable.

In his investigation of the differences of potential between metals and nonaqueous solutions of their salts, Kahlenberg[1] found several cases of reversal of electrode potential, notably in the combinations involving zinc. In the systems

$$Zn—ZnCl_2 \text{ in Quinoline}—ZnCl_2 \text{ in Water}—Zn$$

and

$$Zn—ZnCl_2 \text{ in Ethyl Alcohol}—ZnCl_2 \text{ in Water}—Zn$$

the zinc electrode in the nonaqueous solution was positive.

Commenting on this, Kahlenberg says: "This is very unusual and it is to my knowledge the first case found where zinc is positive toward the solution in which it is immersed."

And again: "I desire once more to call special attention to the fact that while the electromotive force at the contact of a metal and a solution of one of its salts varies with the nature of the solvent, this variation may differ not only as to degree but also as to sense or direction from the potential that the metal exhibits toward, for example, an aqueous solution of the salt." In view of the improbable assumptions involved in any explanation based on the osmotic theory of the voltaic cell it seems unwise at the present time to extend this theory to nonaqueous solutions.

Solution Pressure

The value of the solution pressure of a metal may be calculated by means of equation (1),

$$\pi = \frac{RT}{nF} \log_e \frac{P}{p}$$

Letting $R = 8.32 \times 10^7$ absolute units, $T = 293°$ absolute, $n = 2$, and $F = 96580$ coulombs, and multiplying by 2.3026, the logarithmic modulus, we have

$$\pi = 0.029 \log \frac{P}{p}$$

and

$$\log P = \frac{\pi}{0.029} + \log p$$

[1] *Loc. cit.*

The osmotic pressure of the ions is given by the equation

$$p = m\alpha \times 22.4 \times \frac{293}{273}$$

As the complete expression for P at 20° we have

$$\log P = \frac{\pi}{0.029} + \log 24.04\, m\alpha \qquad (4)$$

The calculation of the solution pressure by means of (4) involves the degree of ionization, α. The values of α for aqueous solutions of cadmium iodide and chloride obtained by the conductivity and the freezing-point methods are not in good agreement, as the following tables (VI and VII) show:

Table VI—Cadmium Iodide in Water at 18°

m	Λ	α^1	α^2 (f. p. method)
1.0	15.4	0.13	....
0.5	18.3	0.15	....
0.2	24.2	0.20	....
0.1	31.0	0.26	0.12
0.05	40.1	0.33	0.23
0.2	53.9	0.45	0.45
0.01	65.6	0.55	0.54

Table VII—Cadmium Chloride in Water at 18°

m	Λ	α^1	α^2 (f. p. method)
1.0	22.4	....	....
0.5	30.8	....	....
0.2	41.2	....	....
0.1	50.0	....	....
0.05	59.0	0.51	0.61
0.02	73.0	0.63	0.75
0.01	83.0	0.72	0.76

With the more dilute solutions the two methods give concordant results and we may venture to employ the values of α for these concentrations in calculating the solution pressure. The results are given in the following table:

[1] Kohlrausch and Holborn: Leitvermögen der Elektrolyte.
[2] Jones: Z. physik. Chem., 11, 544 (1893).

Table VIII

	m	P
Cd in aqueous CdI_2	0.01	5.64×10^5 atmos.
	0.05	1.68×10^6 atmos.
	0.10	1.64×10^6 atmos.
Cd in aqueous $CdCl_2$	0.01	3.45×10^5 atmos.
	0.05	1.07×10^6 atmos.

Comparing these values with the value, $P = 2.7 \times 10^6$ atmospheres, given by Neumann[1] for normal solutions of the chloride, nitrate and sulphate of cadmium, the agreement is perhaps as close as could be expected when we consider the variation among themselves in the above values.

If the Nernst theory is applicable to voltaic combinations in nonaqueous solvents, the value of the solution pressure may be calculated by means of the equation

$$\log P = \frac{\pi}{0.029} + \log p$$

provided the value of p can be determined. In order to calculate p the degree of ionization of the solution must be known. The conductivities of cadmium iodide in methyl and ethyl alcohols have been measured by Zelinsky and Krapiwin[2] and Jones and Carroll,[3] their results being given in Table IX and plotted in Fig. II, together with the values for the conductivity of cadmium iodide and cadmium chloride in aqueous solution. The values of the conductivity are very low and increase but slightly with dilution. While α cannot be obtained by the conductivity method, yet we may infer, from the preceding table and the curves in Fig. II, that the degree of ionization is very small.

Table IX—Cadmium Iodide at 25°

	Methyl alcohol	Ethyl alcohol
v	Λ_v	Λ_v
16	13.07	2.29
32	13.59	2.30
64	14.16	2.32
128	15.01	2.39
256	15.44	2.66

[1] Neumann: Z. physik. Chem., **14,** 193 (1894).
[2] Zelinsky and Krapiwin: *Ibid.*, **31,** 35 (1896).
[3] Jones and Carroll: THIS JOURNAL, **28,** 329 (1902).

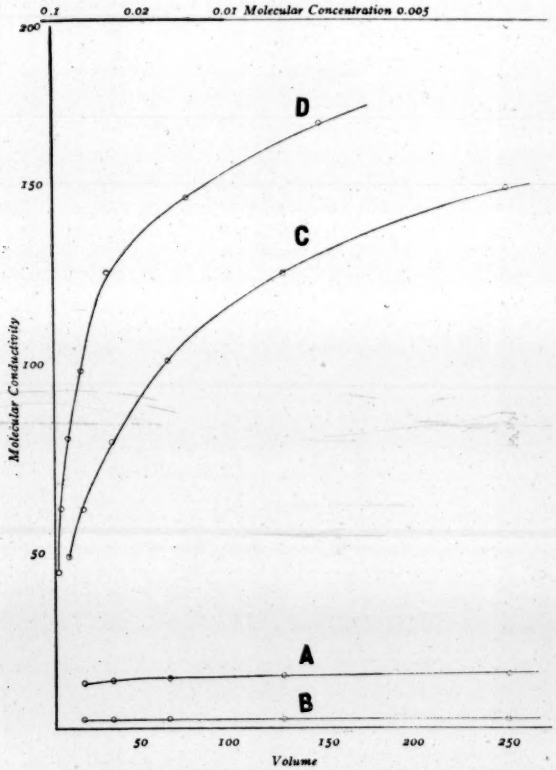

Fig. II.—A. Cadmium iodide in methyl alcohol. B. Cadmium iodide in ethyl alcohol. C. Cadmium iodide in water. D. Cadmium chloride in water.

It having been shown by Jones[1] that the boiling-point method may be employed to measure the ionization in non-aqueous solutions, an attempt was made to determine α for cadmium iodide in both methyl and ethyl alcohols. The small value of the boiling-point constant for methyl alcohol renders the results in this solvent rather unreliable, but it was found that cadmium iodide is partially polymerized in each of the two solvents. The molecular weight of cadmium iodide in methyl alcohol was found to be 702.5 (calculated for CdI_2, 366.24), while in ethyl alcohol it was found to be 687.8. These values are affected by the same errors which we ordinarily associate with molecular-weight determinations by the boiling-point method.

It is evident that at the present time we have no data upon which to base a calculation of the solution pressure of cadmium in the alcohols and furthermore it is doubtful, as has been suggested above, whether the Nernst theory can be applied to nonaqueous solutions, at least without modification. In this connection Kahlenberg[2] says: "If the theory of electrolytic solution tension be held at all, there seems to be no escape from the conclusion that the solution tension varies for different solvents and mixtures of solvents; and hence the dissolved substances—other than the simple ions of the metal in question—may exert an influence in determining the difference of potential between the metal and the solution. If the solution tension changes not only with the solvent, but also with the dissolved substance present, it is questionable, to say the least, whether the hypothesis of an electrolytic solution tension is helpful at all."

It is our intention in the near future to extend the work of which this paper gives a preliminary account.

BRYN MAWR COLLEGE,
May, 1911.

[1] Jones: Z. physik. Chem., **31**, 114 (1899).
[2] Kahlenberg: *Loc. cit.*

CONDUCTIVITY AND VISCOSITY IN MIXED SOLVENTS CONTAINING GLYCEROL

By J. Sam Guy and Harry C. Jones

INTRODUCTION

Jones and Schmidt,[1] in a previous paper published from this laboratory, gave a detailed historical sketch of the work of Jones with Lindsay,[2] Carroll,[3] Bassett,[4] Bingham,[5] Rouiller,[6] McMaster,[7] Veazey,[8] and Mahin,[9] dealing with the relations existing between conductivity and viscosity of a large number of electrolytes in binary mixtures of methyl alcohol, ethyl alcohol, acetone, and water. Schmidt worked with binary mixtures, and introduced glycerol as one of the solvents.

The results of these investigations have been to show that curves representing fluidity and conductivity have, in general, the same form, whether they show maxima or minima as the composition of the mixture is changed.

A fuller discussion of the results and conclusions drawn from the first seven of these investigations has been published as Monograph No. 80 of the Carnegie Institution of Washington (1907). In all of these publications, due credit has been given to previous workers in this field, hence mention of their results need be made only in so far as they bear upon points of interest in this investigation.

The work of Jones and Veazey[10] included a study of the conductivities and fluidities of cupric chloride and potassium sulphocyanate in mixtures of the same general composition as those used by Jones and Bingham.[11] Copper chloride

[1] This Journal, **42**, 37 (1909).
[2] *Ibid.*, **28**, 329 (1902).
[3] *Ibid.*, **32**, 521 (1904).
[4] *Ibid.*, **32**, 409 (1904).
[5] *Ibid.*, **34**, 481 (1905).
[6] *Ibid.*, **36**, 427 (1906).
[7] *Ibid.*, **36**, 325 (1906).
[8] Z. physik. Chem., **61**, 641 (1908).
[9] *Ibid.*, **69**, 389 (1909).
[10] This Journal, **37**, 405 (1907).
[11] *Ibid.*, **34**, 481 (1905).

gave results that were about normal, i. e., the curves representing conductivity and fluidity were very similar.

One of the most interesting points brought out in the investigation of Jones and Veazey was the fact that in certain of the mixtures the solution of potassium sulphocyanate gave *a viscosity that was less than that of the pure solvent.*

Euler[1] had noted that certain salts had the power to lower the viscosity of water, and explained this fact by the aid of the "electrostriction theory" of Drude and Nernst,[2] according to which there exists about every ion, by virtue of its charge, a strong electrostatic field, which causes a strong compression of the liquid in this field.

Wagner and Mühlenbein[3] showed that Euler's reasoning could not hold, since the viscosity of a liquid could be lowered by the addition of certain nonelectrolytes whose viscosity was even greater than that of the solvent. In a word, the effect could not be due to any phenomenon specific to ions, since the molecules could produce the same change.

Jones and Veazey[4] offer a possible explanation of this phenomenon. A careful study of all the viscosity data available showed that only certain salts of potassium, rubidium, and caesium had the power of lowering the viscosity of water. The work of Thorpe and Rodger[5] had indicated that, in all probability, viscosity was a direct function of the skin friction of the ultimate particles present. This being the case, it is not surprising that some salts of the above named metals do not produce this effect, since it is clear that viscosity is an additive property of both the ions present. The one might tend to decrease, the other to increase the viscosity, and the final results would depend upon whether or not the sum of these two opposing influences was positive or negative. These same three metals occupy the maxima on the well-known atomic volume curve of Lothar Meyer.[6] This, of course, means that these metals have very large atomic volumes.

[1] Z. physik. Chem., **25**, 536 (1898).
[2] *Ibid.*, **15**, 79 (1894).
[3] *Ibid.*, **46**, 867 (1903).
[4] THIS JOURNAL, **37**, 405 (1907).
[5] Phil. Trans., **185**, *A*, 307 (1894).
[6] Ann. Chem. (Liebig), Suppl., **7**, 354 (1870).

With these facts at hand, Jones and Veazey offer the following simple explanation as to how any substance may lower the viscosity of the solvent in which it is dissolved. If the atomic volume of the added electrolyte is larger than the molecular aggregates of the solvent, then the relative amount of skin friction in a given volume of solution would be decreased, and hence, according to the hypothesis of Thorpe and Rodger,[1] the viscosity, which is a direct function of the skin friction, would be decreased.

Jones and Veazey use the same reasoning to account for an increase in viscosity when water and alcohol are mixed. Parts of these liquids, as shown by the method of Ramsay and Shields,[2] exist, when pure, in a highly associated condition. Jones and Lindsay,[3] in measuring the conductivities in such a mixture, had noted a minimum conductivity in a mixture containing fifty per cent. of each solvent. In a word, at this point the conductivity was less than that in either solvent independently.

They offer the following explanation. Jones and Murray[4] showed that when two highly associated liquids, which in terms of the hypothesis of Dutoit and Aston[5] would have strong dissociating powers, are mixed, the one breaks down the molecular association of the other. This decrease in association would lessen the power of the solvent to dissociate a given electrolyte into its ions, and thus decrease the conductivity. Jones and Murray actually found that the molecular weights of water, formic acid and acetic acid, when mixed in pairs, showed smaller values than in the pure homogeneous condition. This change in the molecular aggregation would increase the skin friction and thus increase the viscosity.

This lowering of viscosity is of importance as bearing upon some facts established in this investigation, and these will be discussed later.

It is well known that in a strongly dissociating solvent

[1] *Loc. cit.*
[2] Z. physik. Chem., **12,** 433 (1893).
[3] THIS JOURNAL, **28,** 329 (1902).
[4] *Ibid.*, **30,** 193 (1903).
[5] Compt. rend., **125,** 240 (1897).

the conductivity of a ternary electrolyte is, in general, larger than that of a binary one in the same solvent—since there is a larger number of ions present. Jones and Veazey[1] were able to show that potassium sulphocyanate in ethyl alcohol gave a larger molecular conductivity than copper chloride, while in aqueous solution the reverse was true. This, in the opinion of Jones and Veazey, was due to the fact that ethyl alcohol, being a relatively weak dissociating agent, had, at moderate dilutions, the power of breaking copper chloride down into only two ions. This fact will be referred to again under the discussion of the results obtained in this investigation.

Cattaneo[2] measured the conductivities of a few salts in glycerol and found values much smaller than in water. Schettner[3] and Arrhenius[4] measured the viscosities of glycerol and mixtures of this solvent with water and with other nonaqueous solvents. By far the larger part of the work, with glycerol as a solvent, has been done by Jones and Schmidt. The present investigation is a continuation of their work.

Jones and Schmidt have shown that glycerol is an excellent solvent and, in all probability, a fairly good dissociating solvent, since it has a dielectric constant of 16.5 at 18°, and an association factor of 1.8 at the same temperature. With such a dielectric constant and association factor glycerol, according to the Thompson[5]-Nernst[6] and Dutoit and Aston[7] hypotheses, should have a dissociating power approximately equal to that of ethyl alcohol. Jones and Schmidt believed that the extremely small conductivities shown by solutions of electrolytes in glycerol were due to the high viscosity of this solvent.

With these facts before us, an attempt was made to study the relative ionic velocities of electrolytes in glycerol. The apparatus used for this purpose was that devised by Jones and

[1] *Loc. cit.*
[2] Rend. R. Accad. Lincei, [5] **2**, II, 112 (1893).
[3] Wien. Ber., **77**, II 682 (1878).
[4] Z. physik. Chem., **1**, 285 (1887).
[5] Phil. Mag., **36**, 320 (1893).
[6] Z. physik. Chem., **13**, 531 (1894).
[7] *Loc. cit.*

Bassett,[1] and used subsequently in this laboratory.[2] A normal solution of copper chloride in such an apparatus was subjected to a current of 120 volts for forty-eight hours, and only a few milligrams of silver were deposited in the voltameter. Although no final data concerning the migration velocities were obtained, yet the above experiment was sufficient to show that the movement of the ions in solutions of glycerol must be extremely slow as compared with the movement of ions in water and the alcohols, etc.

Jones and Getman[3] had measured the amount of solvation of glycerol in aqueous solution. This work has been repeated and was found to contain an error, probably in the strength of the solution.

The following table shows that the amount of solvation is extremely slight even in the most dilute solutions.

Table A

N	Δ	Δ/m	$W_{sol.}$	$W_{glyc.}$	W_{water}	Cor. Per cent.	L	L'
0.2	0.383	1.91	25.1600	0.4603	24.6997	1.20	1.86	1.89
0.4	0.773	1.93	25.2150	0.9206	24.2944	2.82	1.86	1.88
0.8	1.627	2.03	25.4925	1.8413	23.6512	5.39	1.86	1.92
1.2	2.528	2.10	25.6300	2.7619	22.8681	8.52	1.86	1.92
1.6	3.482	2.18	25.9025	3.6826	22.2199	11.12	1.86	1.94
2.0	4.451	2.22	26.0650	4.6032	21.4618	14.15	1.86	1.90
2.4	5.764	2.34	26.2450	5.5238	20.7212	17.11	1.86	1.64
2.8	6.986	2.46	26.4375	6.4445	19.9930	20.03	1.86	1.95

In this table N is the normality of the solutions, Δ the observed lowering of the freezing point corrected for the separation of ice, Δ/m the molecular lowering of the freezing point, $W_{sol.}$ the weight of 25 cc. of solution, $W_{glyc.}$ the weight of glycerol in 25 cc. of solution, W_{water} the weight of water contained in 25 cc. of solution, L the theoretical molecular lowering of the freezing point referred to 1000 grams of solvent, and L' the observed corrected lowering on the same basis. It is seen that the observed and theoretical molecular lowerings

[1] THIS JOURNAL, **32**, 429 (1904).
[2] *Ibid.*, **36**, 427 (1906).
[3] *Ibid.*, **31**, 303 (1904).

are nearly the same, indicating that the substance does not show any marked hydration in the solutions worked with.

EXPERIMENTAL

Apparatus

In this investigation the Kohlrausch method of measuring conductivity has been employed, the improved Kohlrausch slide-wire bridge, resistance box, induction coil, and telephone receiver being used. The entire apparatus was made and carefully calibrated by Leeds, Northrup and Co., Philadelphia, and, in addition, the standard resistance was checked by the United States Bureau of Standards, Washington, D. C. The new form of bridge is a great improvement over the ordinary Wheatstone bridge, both in convenience and accuracy. By means of such a bridge readings may be checked, under favorable conditions, to one-tenth of a millimeter.

The conductivity cells were of the same type as those described by Jones and Schmidt[1] and Jones and Kreider.[2] Such cells, as has been stated, have very small constants, and hence are well adapted to measuring the conductivity of solutions with high resistances. In every case the cell constants were determined by means of a fiftieth-normal potassium chloride solution, and checks made at frequent intervals showing only slight variations in the cell constants throughout the entire investigation. The molecular conductivity of the fiftieth-normal potassium chloride solution was taken as 129.7 reciprocal Siemens units at 25°.

The constant temperature baths were regulated by electrically-controlled regulators, devised by Reid,[3] and were kept within 0°.02 of the desired temperature. The thermometers were carefully standardized by means of a certificated Reichsanstalt instrument. All flasks, burettes, and other apparatus were carefully calibrated, by weighing, to hold aliquot parts of the true liter at 20°.

[1] *Loc. cit.*
[2] THIS JOURNAL, **45**, 295 (1911).
[3] *Ibid.*, **41**, 148 (1909).

Solutions

For the work at 25°, 35°, and 45°, solutions were made up at 30°, while for the higher temperature work, the solutions were made up at 50°. In all cases the mother solution was made by direct weighing of the carefully dried, anhydrous salt, and from this the N/50 and N/100 solutions were made by dilution. These solutions then served as the mother solutions for the N/200 and N/400, from which, in turn, the N/800 and N/1600 solutions were made. The highest dilution was made by diluting the N/400 solution four times.

Measurements were not made at dilutions higher than sixteen hundred, on account of the extremely high resistance and consequent difficulty in making the readings. In pure glycerol measurements were made at intervals of 5° from 25° to 75°, while in the mixed solvents they were made only at 25°, 35°, and 45°.

Solvents

Glycerol.—The glycerol used was Kahlbaum's best double-distilled product, and had a mean specific conductivity of about 0.9×10^{-7} at 25°. Schmidt had showed that redistillation did not essentially improve the glycerol. Its specific gravity showed that it contained about 0.02 of a per cent. of water. The two lots obtained from Kahlbaum showed somewhat different viscosities, as is indicated in the experimental results.

Water.—The water was purified by the method of Jones and Mackay,[1] with the modification as mentioned by Schmidt, and had a mean specific conductivity of 1.5×10^{-6} at 25°.

Ethyl and Methyl Alcohols.—The ethyl alcohol was purified by several distillations from the very best quality of lime, and block-tin condensers were always used. It had a mean conductivity of 1.8×10^{-7} at 25°. The methyl alcohol was first distilled from a small amount of dilute sulphuric acid and then several times from lime. It had a mean specific conductivity of 2.0×10^{-6} at 25°.

[1] THIS JOURNAL, **17**, 83 (1895).

Salts

In all cases, Kahlbaum's purest articles were used, and these were recrystallized at least three times from conductivity water, carefully dried at 125°, and the solutions made by direct weighing.

Viscosity

The viscosity measurements were made by means of the Ostwald viscosimeter as modified by Jones and Veazey,[1] and the size of the capillary so regulated as to be best adapted to glycerol measurements. The method of calibration has been discussed in detail by Schmidt.[2] Viscosity was calculated from the formula

$$\frac{\eta}{\eta_0} = \frac{St}{S_0 t_0}$$

in which η is the viscosity coefficient for the liquid in question, η_0 that of water, S the specific gravity of the liquid, t the time of flow of the same, S_0 the specific gravity of water at the given temperature, and t_0 the time of flow of the water. Fluidity was calculated from the formula

$$\theta = \frac{1}{\eta}$$

where θ represents the fluidity. The values of η_0 are taken from the work of Thorpe and Rodger,[2] being 0.00891 at 25°, 0.00720 at 35°, 0.00598 at 45°, 0.005057 at 55°, 0.004355 at 65°, and 0.003786 at 75°.

Temperature Coefficients

The temperature coefficients, both in per cent. and in conductivity units, have been calculated, the latter being simply the actual increase in molecular conductivity per degree rise in temperature, while the former were calculated from the formula

$$\text{Temp. coeff. of } \mu_v = \frac{1}{\mu_v 25^\circ} \frac{\mu_v 35^\circ - \mu_v 25^\circ}{10}$$

[1] Z. physik. Chem., **81**, 641 (1908).
[2] *Loc. cit.*

The temperature coefficients of fluidity were calculated in the same way.

Viscosity measurements were made only with the tenth-normal solutions, since at higher dilutions the difference between the viscosity of the solution and that of the solvent was very slight.

Table I—Molecular Conductivity of Potassium Nitrate in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.337	0.681	1.248
50	0.368	0.754	1.384
100	0.373	0.769	1.419
200	0.397	0.818	1.509
400	0.397	0.818	1.510
800	0.412	0.845	1.569
1600	0.431	0.900	1.739

Table II—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1020	0.0833	0.0344	0.0567
50	0.1050	0.0835	0.0386	0.0630
100	0.1061	0.0847	0.0396	0.0650
200	0.1060	0.0845	0.0421	0.0691
400	0.1060	0.0846	0.0421	0.0692
800	0.1051	0.0857	0.0433	0.0724
1600	0.1084	0.0932	0.0469	0.0839

Table III—Molecular Conductivity of Potassium Chloride in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.385	0.772	1.413
50	0.405	0.841	1.516
100	0.412	0.844	1.538
200	0.415	0.850	1.545
400	0.439	0.852	1.571
800	0.443	0.870	1.623
1600	0.536	0.915	1.630

Table IV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1005	0.0830	0.0387	0.0641
50	0.1074	0.0804	0.0436	0.0675
100	0.1048	0.0822	0.0432	0.0694
200	0.1047	0.0818	0.0435	0.0695
400	0.0941	0.0844	0.0413	0.0719
800	0.0964	0.0865	0.0427	0.0753
1600	0.0708	0.0781	0.0379	0.0715

Table V—Molecular Conductivity of Potassium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.366	0.752	1.376
50	0.369	0.752	1.396
100	0.384	0.778	1.434
200	0.385	0.782	1.435
400	0.386	0.801	1.527
800	0.390	0.821	1.578
1600	0.413	0.877	1.667

Table VI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1054	0.0829	0.0386	0.0624
50	0.1041	0.0857	0.0383	0.0644
100	0.1028	0.0843	0.0394	0.0656
200	0.1031	0.0835	0.0397	0.0653
400	0.1080	0.0906	0.0415	0.0726
800	0.1104	0.0922	0.0431	0.0757
1600	0.1123	0.0901	0.0464	0.0790

Table VII—Molecular Conductivity of Sodium Chloride in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.328	0.666	1.223
50	0.351	0.711	1.319
100	0.353	0.720	1.350
200	0.372	0.753	1.409
400	0.375	0.765	1.421
800	0.391	0.806	1.588
1600	0.395	0.825	1.629

Table VIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1030	0.0838	0.0338	0.0557
50	0.1024	0.0855	0.0360	0.0608
100	0.1038	0.0872	0.0367	0.0630
200	0.1024	0.0871	0.0381	0.0656
400	0.1040	0.0856	0.0390	0.0656
800	0.1061	0.0970	0.0415	0.0782
1600	0.1090	0.0974	0.0430	0.0804

Table IX—Molecular Conductivity of Sodium Iodide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.342	0.690	1.265
50	0.364	0.737	1.361
100	0.366	0.745	1.372
200	0.379	0.761	1.397
400	0.397	0.786	1.452
800	0.388	0.760	1.418
1600	0.447	0.840	1.557

Table X—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1047	0.0833	0.0348	0.0575
50	0.1021	0.0846	0.0373	0.0624
100	0.1035	0.0841	0.0379	0.0627
200	0.1019	0.0836	0.0382	0.0636
400	0.0978	0.0847	0.0389	0.0666
800	0.0959	0.0865	0.0372	0.0658
1600	0.0879	0.0853	0.0393	0.0717

Table XI—Molecular Conductivity of Sodium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.318	0.646	1.192
50	0.331	0.678	1.260
100	0.332	0.682	1.293
200	0.359	0.734	1.367
400	0.363	0.754	1.410
800	0.379	0.784	1.465
1600	0.384	0.791	1.515

Table XII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1034	0.0846	0.0328	0.0546
50	0.1046	0.0864	0.0347	0.0582
100	0.1054	0.0884	0.0350	0.0611
200	0.1042	0.0868	0.0375	0.0633
400	0.1077	0.0870	0.0391	0.0656
800	0.1067	0.0869	0.0405	0.0681
1600	0.1068	0.0913	0.0407	0.0724

Table XIII—Molecular Conductivity of Sodium Nitrate in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.303	0.617	1.129
50	0.331	0.677	1.239
100	0.338	0.707	1.284
200	0.355	0.735	1.362
400	0.358	0.737	1.378
800	0.372	0.766	1.412
1600	0.386	0.796	1.544

Table XIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1033	0.0828	0.0314	0.0512
50	0.1046	0.0830	0.0346	0.0562
100	0.1096	0.0818	0.0369	0.0577
200	0.1070	0.0851	0.0380	0.0627
400	0.1058	0.0870	0.0379	0.0641
800	0.1058	0.0843	0.0394	0.0646
1600	0.1062	0.0940	0.0410	0.0748

Table XV—Molecular Conductivity of Ammonium Chloride in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.393	0.801	1.452
50	0.411	0.849	1.543
100	0.426	0.879	1.605
200	0.427	0.889	1.623
400	0.432	0.889	1.639
800	0.440	0.931	1.696
1600	0.442	0.948	1.709

Table XVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1038	0.0812	0.0408	0.0651
50	0.1065	0.0808	0.0438	0.0694
100	0.1063	0.0827	0.0453	0.0726
200	0.1080	0.0825	0.0462	0.0734
400	0.1057	0.0844	0.0457	0.0750
800	0.1113	0.0822	0.0491	0.0765
1600	0.1123	0.0803	0.0506	0.0761

Table XVII—Molecular Conductivity of Ammonium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.373	0.758	1.391
50	0.391	0.802	1.490
100	0.397	0.824	1.531
200	0.422	0.878	1.632
400	0.430	0.889	1.642
800	0.444	0.926	1.694
1600	0.492	1.034	1.864

Table XVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1032	0.0835	0.0385	0.0633
50	0.1051	0.0850	0.0411	0.0688
100	0.1075	0.0856	0.0427	0.0707
200	0.1075	0.0862	0.0456	0.0754
400	0.1069	0.0847	0.0459	0.0753
800	0.1092	0.0829	0.0482	0.0768
1600	0.1102	0.0803	0.0542	0.0830

Table XIX—Molecular Conductivity of Ammonium Nitrate in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.345	0.696	1.272
50	0.379	0.778	1.440
100	0.392	0.805	1.488
200	0.407	0.840	1.547
400	0.417	0.869	1.594
800	0.396	0.825	1.579
1600	0.437	0.917	1.651

Table XX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1020	0.0832	0.0351	0.0576
50	0.1053	0.0851	0.0399	0.0662
100	0.1058	0.0850	0.0413	0.0683
200	0.1063	0.0844	0.0433	0.0707
400	0.1084	0.0835	0.0452	0.0725
800	0.1084	0.0914	0.0429	0.0754
1600	0.1095	0.0802	0.0480	0.0734

Table XXI—Molecular Conductivity of Barium Chloride in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.315	0.664	1.221
50	0.432	0.915	1.695
100	0.464	0.978	1.803
200	0.502	1.056	1.951
400	0.520	1.101	1.994
800	0.561	1.197	2.230
1600	0.565	1.332	2.368

Table XXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1108	0.0839	0.0349	0.0557
50	0.1115	0.0853	0.0483	0.0780
100	0.1108	0.0844	0.0514	0.0825
200	0.1103	0.0852	0.0554	0.0895
400	0.1116	0.0811	0.0581	0.0893
800	0.1134	0.0863	0.0636	0.1033
1600	0.1358	0.0778	0.0767	0.1036

Table XXIII—Molecular Conductivity of Barium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.330	0.696	1.314
50	0.396	0.832	1.566
100	0.426	0.900	1.698
200	0.443	0.938	1.774
400	0.474	1.001	1.896
800	0.520	1.127	2.115
1600	0.530	1.157	2.200

Table XXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1109	0.0888	0.0366	0.0618
50	0.1101	0.0882	0.0436	0.0734
100	0.1112	0.0887	0.0474	0.0798
200	0.1117	0.0894	0.0495	0.0836
400	0.1112	0.0894	0.0527	0.0895
800	0.1160	0.0876	0.0607	0.0988
1600	0.1180	0.0900	0.0627	0.1043

Table XXV—Molecular Conductivity of Barium Nitrate in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.246	0.517	0.959
50	0.347	0.738	1.367
100	0.368	0.792	1.479
200	0.401	0.871	1.634
400	0.414	0.904	1.719
800	0.456	0.988	1.871
1600	0.462	0.991	1.897

Table XXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1101	0.0854	0.0271	0.0442
50	0.1126	0.0852	0.0391	0.0629
100	0.1152	0.0867	0.0424	0.0687
200	0.1170	0.0876	0.0470	0.0763
400	0.1168	0.0901	0.0490	0.0815
800	0.1166	0.0893	0.0532	0.0883
1600	0.1145	0.0914	0.0529	0.0906

Table XXVII—Molecular Conductivity of Calcium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.245	0.519	0.972
50	0.324	0.687	1.298
100	0.340	0.729	1.374
200	0.373	0.803	1.514
400	0.386	0.833	1.556
800	0.395	0.882	1.721
1600	0.408	0.909	1.743

Table XXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1118	0.0873	0.0274	0.0453
50	0.1120	0.0888	0.0363	0.0611
100	0.1144	0.0883	0.0389	0.0645
200	0.1152	0.0886	0.0430	0.0711
400	0.1157	0.0891	0.0447	0.0723
800	0.1233	0.0951	0.0487	0.0839
1600	0.1226	0.0918	0.0501	0.0834

Table XXIX—Molecular Conductivity of Strontium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.264	0.556	1.054
50	0.340	0.717	1.362
100	0.365	0.776	1.468
200	0.388	0.831	1.581
400	0.391	0.876	1.659
800	0.409	0.886	1.681
1600	0.428	0.924	1.758

Table XXX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1106	0.0895	0.0292	0.0498
50	0.1118	0.0899	0.0377	0.0645
100	0.1126	0.0892	0.0411	0.0692
200	0.1133	0.0903	0.0443	0.0750
400	0.1189	0.0893	0.0485	0.0783
800	0.1166	0.0895	0.0477	0.0795
1600	0.1162	0.0902	0.0496	0.0834

Table XXXI—Molecular Conductivity of Strontium Nitrate in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.235	0.501	0.934
50	0.323	0.687	1.292
100	0.349	0.744	1.394
200	0.392	0.833	1.563
400	0.401	0.872	1.686
800	0.411	0.891	1.671
1600	0.449	0.945	1.759

Table XXXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1127	0.0864	0.0266	0.0433
50	0.1121	0.0885	0.0364	0.0605
100	0.1131	0.0871	0.0395	0.0650
200	0.1121	0.0876	0.0441	0.0730
400	0.1173	0.0933	0.0471	0.0814
800	0.1170	0.0874	0.0480	0.0780
1600	0.1102	0.0861	0.0496	0.0814

Table XXXIII—Molecular Conductivity of Cobalt Chloride in Glycerol at 25°, 35°, 45°[1]

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.270	0.546	1.003
50	0.369	0.744	1.373
100	0.391	0.784	1.450
200	0.455	0.911	1.691
400	0.473	0.959	1.779
800	0.497	1.005	1.856
1600	0.519	1.040	1.920

Table XXXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1023	0.0836	0.0276	0.0457
50	0.1015	0.0846	0.0375	0.0629
100	0.1004	0.0849	0.0393	0.0666
200	0.1004	0.0857	0.0456	0.0780
400	0.1027	0.0855	0.0486	0.0820
800	0.1022	0.0847	0.0508	0.0851
1600	0.1002	0.0846	0.0521	0.0880

Table XXXV—Molecular Conductivity of Cobalt Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.364	0.744	1.370
50	0.460	0.932	1.702
100	0.468	0.953	1.743
200	0.514	1.045	1.911
400	0.533	1.076	1.967
800	0.552	1.103	2.031
1600	0.564	1.091	2.005

[1] Schmidt.

Table XXXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1043	0.0841	0.0380	0.0626
50	0.1026	0.0826	0.0472	0.0770
100	0.1036	0.0829	0.0485	0.0790
200	0.1032	0.0827	0.0531	0.0866
400	0.1021	0.0827	0.0543	0.0891
800	0.0998	0.0841	0.0551	0.0928
1600	0.0934	0.0837	0.0527	0.0914

Table XXXVII—Molecular Conductivity of Potassium Chloride in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.391	3.755	5.601
50	2.601	4.124	6.176
100	2.707	4.252	6.300
200	2.734	4.341	6.489
400	2.738	4.470	6.691
800	2.817	4.562	6.862
1600	2.940	4.693	6.891

Table XXXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0570	0.0491	0.1364	0.1846
50	0.0586	0.0497	0.1523	0.2052
100	0.0571	0.0482	0.1545	0.2048
200	0.0588	0.0496	0.1607	0.2148
400	0.0632	0.0499	0.1732	0.2221
800	0.0623	0.0504	0.1745	0.2300
1600	0.0596	0.0470	0.1753	0.2198

Table XXXIX—Molecular Conductivity of Potassium Bromide in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.293	3.619	5.332
50	2.453	3.906	4.786
100	2.557	4.062	6.080
200	2.606	4.122	6.154
400	2.680	4.275	6.317
800	2.705	4.286	6.408
1600	2.770	4.400	6.897

Table XL—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0576	0.0473	0.1326	0.1713
50	0.0592	0.0481	0.1453	0.1880
100	0.0587	0.0496	0.1505	0.2018
200	0.0572	0.0493	0.1516	0.2032
400	0.0594	0.0477	0.1595	0.2042
800	0.0584	0.0496	0.1581	0.2122
1600	0.0588	0.0568	0.1630	0.2497

Table XLI—Molecular Conductivity of Sodium Bromide in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.006	3.153	4.763
50	2.203	3.500	5.262
100	2.299	3.656	5.504
200	2.325	3.683	5.566
400	2.397	3.715	5.753
800	2.438	3.760	5.864
1600	2.493	3.965	5.938

Table XLII—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0570	0.0510	0.1147	0.1610
50	0.0588	0.0503	0.1297	0.1762
100	0.0590	0.0505	0.1357	0.1848
200	0.0584	0.0511	0.1358	0.1883
400	0.0550	0.0548	0.1318	0.2038
800	0.0542	0.0559	0.1322	0.2104
1600	0.0590	0.0497	0.1472	0.1973

Table XLIII—Molecular Conductivity of Sodium Iodide in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.101	3.300	4.878
50	2.246	3.568	5.407
100	2.347	3.731	5.590
200	2.377	3.756	5.604
400	2.441	3.865	5.822
800	2.410	3.833	5.745
1600	2.591	4.263	6.415

Table XLIV—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0570	0.0478	0.1199	0.1578
50	0.0588	0.0515	0.1322	0.1839
100	0.0589	0.0498	0.1384	0.1859
200	0.0581	0.0492	0.1379	0.1848
400	0.0584	0.0506	0.1424	0.1957
800	0.0591	0.0498	0.1423	0.1912
1600	0.0644	0.0644	0.1672	0.2152

Table XLV—Molecular Conductivity of Ammonium Chloride in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.785	4.313	6.285
50	2.863	4.498	6.593
100	3.109	4.821	7.033
200	3.144	4.789	7.018
400	3.146	4.858	7.162
800	3.252	5.051	7.409
1600	3.224	5.015	7.351

Table XLVI—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0545	0.0457	0.1528	0.1972
50	0.0571	0.0466	0.1635	0.2095
100	0.0550	0.0459	0.1712	0.2212
200	0.0523	0.0465	0.1645	0.2229
400	0.0544	0.0465	0.1712	0.2304
800	0.0553	0.0466	0.1799	0.2358
1600	0.0557	0.0465	0.1791	0.2336

Table XLVII—Molecular Conductivity of Ammonium Nitrate in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.558	3.942	5.873
50	2.766	4.250	6.310
100	2.907	4.458	6.772
200	2.947	4.580	6.844
400	3.015	4.661	6.956
800	3.103	4.754	7.107
1600	3.194	4.923	8.372

Table XLVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0541	0.0489	0.1384	0.1931
50	0.0536	0.0485	0.1484	0.2060
100	0.0533	0.0519	0.1551	0.2314
200	0.0554	0.0494	0.1633	0.2264
400	0.0545	0.0492	0.1646	0.2295
800	0.0532	0.0494	0.1651	0.2353
1600	0.0541	0.0497	0.1729	0.2449

Table XLIX—Molecular Conductivity of Barium Nitrate in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.262	3.565	5.300
50	2.856	4.480	6.725
100	3.106	4.906	7.304
200	3.362	5.269	7.858
400	3.555	5.629	8.555
800	3.757	5.987	9.046
1600	3.942	6.236	9.466

Table L—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0576	0.0486	0.1303	0.1735
50	0.0569	0.0499	0.1624	0.2245
100	0.0579	0.0491	0.1800	0.2394
200	0.0567	0.0491	0.1907	0.2589
400	0.0579	0.0519	0.2074	0.2926
800	0.0593	0.0511	0.2230	0.3059
1600	0.0581	0.0517	0.2294	0.3230

Table LI—Molecular Conductivity of Strontium Chloride in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.243	3.576	5.378
50	2.727	4.312	6.442
100	2.900	4.610	6.880
200	3.101	4.946	7.423
400	3.314	5.257	7.855
800	3.389	5.400	8.078
1600	3.645	5.750	8.780

Table LII—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0594	0.0503	0.1333	0.1802
50	0.0581	0.0493	0.1585	0.2130
100	0.0589	0.0492	0.1710	0.2270
200	0.0592	0.0501	0.1845	0.2477
400	0.0587	0.0494	0.1943	0.2598
800	0.0593	0.0495	0.2011	0.2678
1600	0.0577	0.0527	0.2105	0.3030

Table LIII—Molecular Conductivity of Cobalt Chloride in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	1.789	2.778	4.102
50	2.373	3.686	5.447
100	2.610	4.074	6.024
200	2.890	4.513	6.687
400	3.104	4.864	7.236
800	3.286	5.178	7.750
1600	3.471	5.503	8.247

Table LIV—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0553	0.0476	0 0989	0.1324
50	0.0553	0.0477	0.1313	0.1761
100	0.0560	0.0478	0.1464	0.1950
200	0.0561	0.0481	0.1623	0.2174
400	0.0566	0.0487	0.1760	0.2372
800	0.0575	0.0496	0.1892	0.2572
1600	0.0585	0.0497	0.2032	0.2744

Table LV—Molecular Conductivity of Cobalt Bromide in Glycerol at 55°, 65°, 75°

V	μ_v 55°	μ_v 65°	μ_v 75°
10	2.340	3.676	5.462
50	2.905	4.561	6.841
100	2.952	4.628	6.954
200	3.229	5.068	7.584
400	3.338	5.242	7.904
800	3.429	5.420	8.549
1600	3.400	5.399	8.112

Table LVI—Temperature Coefficients

	Per cent.		Cond. units	
V	55°–65°	65°–75°	55°–65°	65°–75°
10	0.0571	0.0485	0.1336	0.1786
50	0.0571	0.0499	0.1656	0.2280
100	0.0568	0.0503	0.1676	0.2326
200	0.0569	0.0496	0.1839	0.2516
400	0.0572	0.0511	0.1904	0.2662
800	0.0582	0.0596	0.1991	0.3129
1600	0.0588	0.0508	0.1999	0.2713

Table LVII—Molecular Conductivity of Potassium Chloride in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.385	0.772	1.413
50	0.405	0.841	1.516
100	0.412	0.844	1.538
200	0.415	0.850	1.545
400	0.439	0.852	1.571
800	0.443	0.870	1.623
1600	0.536	0.915	1.630

Table LVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1006	0.0830	0.0387	0.0641
50	0.1074	0.0804	0.0436	0.0675
100	0.1049	0.0822	0.0432	0.0694
200	0.1047	0.0818	0.0435	0.0695
400	0.0948	0.0842	0.0413	0.0719
800	0.0962	0.0865	0.0427	0.0753
1600	0.0707	0.0781	0.0379	0.0715

Table LIX—Molecular Conductivity of Potassium Chloride in a Mixture of 75 Per cent. Glycerol with Water at 25°, 35, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	5.33	8.29	11.92
50	5.78	9.00	13.04
100	5.86	9.08	13.09
200	6.07	9.39	13.71
400	6.38	9.89	14.47
800	6.61	10.27	14.66
1600	6.51	10.15	14.92

Table LX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0554	0.0438	0.296	0.363
50	0.0556	0.0449	0.322	0.404
100	0.0549	0.0441	0.322	0.401
200	0.0548	0.0460	0.332	0.432
400	0.0550	0.0463	0.351	0.458
800	0.0553	0.0427	0.366	0.439
1600	0.0558	0.0469	0.364	0.477

Table LXI—Molecular Conductivity of Potassium Chloride in a Mixture of 50 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	23.55	31.59	40.28
50	25.17	33.89	43.84
100	26.00	34.73	45.68
200	26.30	35.17	45.73
400	28.52	38.35	49.63
800	29.21	39.28	50.37
1600	30.57	41.12	52.33

Table LXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0341	0.0275	0.804	0.869
50	0.0345	0.0294	0.872	0.995
100	0.0336	0.0316	0.873	1.095
200	0.0338	0.0300	0.887	1.056
400	0.0344	0.0294	0.983	1.128
800	0.0344	0.0282	1.007	1.109
1600	0.0345	0.0273	1.055	1.121

Table LXIII—Molecular Conductivity of Potassium Chloride in a Mixture of 25 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	59.81	74.52	90.16
50	65.00	81.89	98.63
100	66.68	82.94	101.08
200	68.13	85.34	103.36
400	74.87	93.04	112.24
800	77.85	96.30	116.68
1600	78.99	98.98	121.32

Table LXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0246	0.0212	1.471	1.564
50	0.0258	0.0204	1.689	1.674
100	0.0244	0.0216	1.626	1.814
200	0.0253	0.0211	1.721	1.802
400	0.0243	0.0206	1.817	1.920
800	0.0238	0.0213	1.845	2.038
1600	0.0253	0.0226	1.999	2.234

Table LXV—Molecular Conductivity of Potassium Chloride in Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	120.4	143.0	166.7
50	129.7	154.5	181.2
100	132.0	158.5	184.7
200	135.3	161.6	189.3
400	137.7	165.4	193.8
800	138.1	165.8	194.8
1600	140.3	169.3	197.9

Table LXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0188	0.0158	2.26	2.37
50	0.0192	0.0171	2.48	2.67
100	0.0200	0.0166	2.65	2.62
200	0.0195	0.0171	2.63	2.77
400	0.0201	0.0171	2.77	2.84
800	0.0201	0.0174	2.77	2.90
1600	0.0206	0.0169	2.90	2.86

Table LXVII—Molecular Conductivity of Potassium Chloride in a Mixture of 75 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	1.21	2.05	3.26
50	1.31	2.25	3.59
100	1.35	2.34	3.69
200	1.41	2.43	3.90
400	1.53	2.63	4.22
800	1.54	2.67	4.27
1600	1.59	2.72	4.32

Table LXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0694	0.0590	0.084	0.121
50	0.0717	0.0596	0.094	0.134
100	0.0733	0.0577	0.099	0.135
200	0.0723	0.0605	0.102	0.147
400	0.0719	0.0605	0.110	0.159
800	0.0733	0.0599	0.113	0.160
1600	0.0710	0.0588	0.113	0.160

Table LXIX—Molecular Conductivity of Potassium Chloride in a Mixture of 50 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	3.07	4.48	6.29
50	3.54	5.21	7.38
100	3.76	5.63	7.86
200	4.09	5.94	8.37
400	4.40	6.56	9.27
800	4.52	6.76	9.61
1600	4.62	6.84	9.79

Table LXX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0459	0.0404	0.141	0.181
50	0.0471	0.0420	0.167	0.217
100	0.0500	0.0396	0.187	0.223
200	0.0451	0.0409	0.185	0.243
400	0.0490	0.0413	0.216	0.271
800	0.0491	0.0421	0.224	0.295
1600	0.0481	0.0431	0.222	0.295

Table LXXI—Molecular Conductivity of Potassium Chloride in a Mixture of 25 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	7.26	9.31	11.94
50	8.31	10.78	13.61
100	9.29	12.15	15.39
200	9.97	13.02	16.61
400	11.32	15.31	19.15
800	11.88	15.68	20.28
1600	12.37	16.31	21.06

Table LXXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0281	0.0282	0.205	0.263
50	0.0297	0.0262	0.247	0.283
100	0.0308	0.0267	0.286	0.324
200	0.0306	0.0276	0.305	0.359
400	0.0352	0.0251	0.399	0.384
800	0.0320	0.0293	0.380	0.460
1600	0.0319	0.0281	0.394	0.475

Table LXXIII—Molecular Conductivity of Potassium Chloride in a Mixture of 75 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	2.22	3.58	5.43
50	2.41	3.93	5.91
100	2.47	4.07	6.11
200	2.58	4.21	6.38
400	2.78	4.52	6.88
800	2.83	4.64	7.07
1600	2.83	4.62	6.99

Table LXXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0612	0.0517	0.136	0.185
50	0.0630	0.0505	0.152	0.198
100	0.0640	0.0500	0.160	0.204
200	0.0632	0.0515	0.163	0.217
400	0.0625	0.0522	0.174	0.236
800	0.0639	0.0524	0.181	0.243
1600	0.0632	0.0515	0.179	0.237

Table LXXV—Molecular Conductivity of Potassium Chloride in a Mixture of 50 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	8.10	11.09	14.54
50	9.24	12.75	16.71
100	9.59	13.17	17.48
200	10.05	13.77	18.22
400	11.04	15.20	20.17
800	11.20	15.34	20.41
1600	11.38	15.63	20.64

Table LXXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0369	0.0311	0.299	0.345
50	0.0378	0.0311	0.351	0.396
100	0.0374	0.0326	0.358	0.431
200	0.0375	0.0323	0.372	0.445
400	0.0376	0.0324	0.416	0.497
800	0.0371	0.0330	0.414	0.507
1600	0.0365	0.0321	0.425	0.501

Table LXXVII—Molecular Conductivity of Potassium Chloride in a Mixture of 25 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	21.76	26.55	31.11
50	25.85	31.45	37.75
100	27.57	33.65	40.36
200	28.72	35.34	42.30
400	31.01	38.19	45.51
800	33.15	40.70	48.85
1600	33.99	42.05	49.55

Table LXXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0220	0.0172	0.479	0.456
50	0.0218	0.0200	0.560	0.630
100	0.0221	0.0199	0.608	0.671
200	0.0230	0.0197	0.662	0.696
400	0.0231	0.0193	0.718	0.732
800	0.0227	0.0200	0.755	0.815
1600	0.0237	0.0179	0.806	0.750

Table LXXIX—Molecular Conductivity of Sodium Nitrate in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.303	0.617	1.129
50	0.331	0.677	1.239
100	0.338	0.707	1.284
200	0.355	0.735	1.362
400	0.358	0.737	1.378
800	0.372	0.766	1.412
1600	0.386	0.796	1.544

Table LXXX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1033	0.0828	0.0314	0.0512
50	0.1046	0.0830	0.0346	0.0562
100	0.1096	0.0816	0.0369	0.0577
200	0.1070	0.0853	0.0380	0.0627
400	0.1058	0.0869	0.0379	0.0641
800	0.1058	0.0843	0.0394	0.0646
1600	0.1062	0.0939	0.0410	0.0748

Table LXXXI—Molecular Conductivity of Sodium Nitrate in a Mixture of 75 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	4.88	7.46	10.80
50	5.37	8.39	12.03
100	5.45	8.44	12.33
200	5.63	8.68	12.58
400	6.09	9.35	13.65
800	6.34	9.75	14.20
1600	6.37	9.75	14.34

Table LXXXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0529	0.0448	0.258	0.334
50	0.0561	0.0434	0.302	0.364
100	0.0549	0.0460	0.299	0.389
200	0.0541	0.0449	0.305	0.390
400	0.0534	0.0459	0.326	0.430
800	0.0538	0.0455	0.341	0.445
1600	0.0531	0.0471	0.338	0.459

Table LXXXIII—Molecular Conductivity of Sodium Nitrate in a Mixture of 50 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	18.87	25.41	33.03
50	20.60	27.84	36.08
100	21.26	28.79	37.35
200	21.46	29.34	37.98
400	21.69	29.63	38.42
800	23.73	31.74	42.17
1600	24.53	32.57	43.69

Table LXXXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0348	0.0298	0.654	0.762
50	0.0350	0.0298	0.724	0.824
100	0.0352	0.0297	0.753	0.856
200	0.0367	0.0295	0.788	0.864
400	0.0365	0.0294	0.794	0.879
800	0.0338	0.0329	0.801	1.043
1600	0.0329	0.0341	0.804	1.112

Table LXXXV—Molecular Conductivity of Sodium Nitrate in a Mixture of 25 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	48.19	60.40	73.81
50	52.17	64.90	80.77
100	53.65	68.25	82.75
200	54.47	69.18	84.41
400	55.25	69.74	86.03
800	60.09	75.35	93.20
1600	62.03	77.90	96.30

Table LXXXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0253	0.0222	1.221	1.341
50	0.0244	0.0244	1.273	1.587
100	0.0272	0.0213	1.460	1.450
200	0.0267	0.0221	1.471	1.523
400	0.0264	0.0233	1.449	1.629
800	0.0254	0.0236	1.526	1.785
1600	0.0254	0.0235	1.587	1.840

Table LXXXVII—Molecular Conductivity of Sodium Nitrate in Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	94.7	113.4	133.2
50	103.8	125.0	147.5
100	104.7	127.0	149.5
200	107.8	130.5	153.2
400	113.7	135.3	159.6
800	113.0	135.8	160.1
1600	116.0	142.6	169.7

Table LXXXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0198	0.0175	1.87	1.98
50	0.0204	0.0180	2.12	2.25
100	0.0212	0.0176	2.23	2.25
200	0.0211	0.0174	2.27	2.27
400	0.0190	0.0179	2.16	2.43
800	0.0201	0.0179	2.28	2.43
1600	0.0230	0.0190	2.66	2.71

Table LXXXIX—Molecular Conductivity of Sodium Nitrate in a Mixture of 75 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	1.02	1.77	2.79
50	1.17	1.99	3.20
100	1.20	2.09	3.30
200	1.26	2.19	3.51
400	1.38	2.37	3.75
800	1.39	2.43	3.84
1600	1.39	2.42	3.87

Table XC—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0736	0.0576	0.075	0.102
50	0.0701	0.0605	0.082	0.121
100	0.0742	0.0576	0.089	0.121
200	0.0739	0.0602	0.093	0.132
400	0.0721	0.0582	0.099	0.138
800	0.0746	0.0579	0.104	0.141
1600	0.0742	0.0600	0.103	0.145

Table XCI—Molecular Conductivity of Sodium Nitrate in a Mixture of 50 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	3.08	4.49	6.20
50	3.68	5.41	7.58
100	3.89	5.74	8.07
200	4.04	6.00	8.44
400	4.52	6.67	9.49
800	4.70	6.95	9.78
1600	4.80	7.14	10.18

Table XCII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0457	0.0381	0.141	0.171
50	0.0470	0.0400	0.173	0.217
100	0.0475	0.0406	0.185	0.233
200	0.0478	0.0406	0.196	0.244
400	0.0475	0.0422	0.215	0.282
800	0.0478	0.0393	0.225	0.273
1600	0.0487	0.0426	0.234	0.304

Table XCIII—Molecular Conductivity of Sodium Nitrate in a Mixture of 25 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	7.36	9.45	11.74
50	9.75	12.56	15.65
100	10.57	13.65	17.33
200	11.50	14.85	18.87
400	12.89	16.85	21.34
800	13.74	17.71	22.38
1600	14.00	18.36	22.72

Table XCIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0284	0.0243	0.209	0.229
50	0.0288	0.0246	0.281	0.309
100	0.0292	0.0269	0.308	0.368
200	0.0290	0.0270	0.335	0.402
400	0.0305	0.0268	0.396	0.449
800	0.0288	0.0261	0.397	0.468
1600	0.0305	0.0244	0.436	0.436

Table XCV—Molecular Conductivity of Sodium Nitrate in a Mixture of 75 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	1.86	2.99	4.54
50	2.07	3.42	5.31
100	2.17	3.58	5.43
200	2.24	3.64	5.62
400	2.41	3.99	6.02
800	2.53	4.08	6.24
1600	2.49	4.13	6.26

Table XCVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0603	0.0519	0.113	0.155
50	0.0652	0.0552	0.135	0.189
100	0.0650	0.0521	0.141	0.185
200	0.0714	0.0544	0.160	0.198
400	0.0654	0.0510	0.158	0.203
800	0.0613	0.0532	0.155	0.216
1600	0.0658	0.0515	0.164	0.213

Table XCVII—Molecular Conductivity of Sodium Nitrate in a Mixture of 50 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	7.35	10.02	13.25
50	8.68	11.88	15.69
100	9.09	12.53	16.47
200	9.59	13.22	17.53
400	10.44	14.46	19.06
800	10.75	14.87	19.57
1600	10.80	15.08	19.57

Table XCVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0363	0.0315	0.267	0.323
50	0.0368	0.0320	0.320	0.381
100	0.0377	0.0314	0.344	0.394
200	0.0378	0.0304	0.363	0.431
400	0.0385	0.0318	0.402	0.460
800	0.0383	0.0316	0.412	0.470
1600	0.0390	0.0293	0.428	0.449

Table XCIX—Molecular Conductivity of Sodium Nitrate in a Mixture of 25 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	20.77	25.22	30.59
50	25.71	31.35	37.47
100	27.59	33.81	40.31
200	28.81	35.27	42.19
400	30.06	36.88	44.45
800	33.11	40.42	48.20
1600	34.00	41.82	49.78

Table C—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0214	0.0210	0.445	0.537
50	0.0223	0.0198	0.564	0.612
100	0.0224	0.0198	0.622	0.650
200	0.0220	0.0196	0.646	0.692
400	0.0225	0.0205	0.682	0.757
800	0.0218	0.0192	0.731	0.778
1600	0.0230	0.0191	0.782	0.796

Table CI—Molecular Conductivity of Ammonium Bromide in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.373	0.758	1.391
50	0.391	0.802	1.490
100	0.397	0.824	1.531
200	0.422	0.878	1.632
400	0.430	0.889	1.642
800	0.444	0.926	1.694
1600	0.492	1.034	1.864

Table CII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1032	0.0838	0.0385	0.0633
50	0.1051	0.0850	0.0411	0.0688
100	0.1075	0.0850	0.0427	0.0707
200	0.1080	0.0862	0.0456	0.0754
400	0.1069	0.0847	0.0459	0.0753
800	0.1085	0.0829	0.0482	0.0768
1600	0.1106	0.0802	0.0542	0.0830

Table CIII—Molecular Conductivity of Ammonium Bromide in a Mixture of 75 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	5.53	8.48	12.28
50	5.91	9.14	13.26
100	5.97	9.25	13.30
200	6.17	9.54	13.83
400	6.62	10.28	14.87
800	6.95	10.81	15.45
1600	7.29	11.20	15.88

Table CIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0536	0.0448	0.295	0.380
50	0.0546	0.0450	0.323	0.412
100	0.0548	0.0429	0.328	0.405
200	0.0546	0.0446	0.337	0.429
400	0.0553	0.0446	0.366	0.459
800	0.0555	0.0429	0.386	0.464
1600	0.0538	0.0420	0.391	0.468

Table CV—Molecular Conductivity of Ammonium Bromide in a Mixture of 50 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	24.31	32.58	42.06
50	25.74	34.54	44.59
100	26.62	35.61	45.65
200	27.01	36.12	46.44
400	27.86	37.32	47.87
800	30.20	40.54	52.33
1600	32.58	43.00	54.79

Table CVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0340	0.0291	0.827	0.948
50	0.0341	0.0290	0.880	1.005
100	0.0340	0.0282	0.899	1.004
200	0.0334	0.0285	0.911	1.032
400	0.0339	0.0278	0.946	1.055
800	0.0342	0.0288	1.034	1.179
1600	0.0325	0.0275	1.042	1.179

Table CVII—Molecular Conductivity of Ammonium Bromide in a Mixture of 25 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	61.45	76.93	92.72
50	66.55	83.43	101.38
100	67.68	84.90	103.56
200	69.32	86.80	104.52
400	70.69	88.08	106.74
800	71.29	89.82	108.68
1600	71.34	89.58	107.96

Table CVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0249	0.0205	1.548	1.579
50	0.0254	0.0215	1.688	1.795
100	0.0255	0.0218	1.722	1.866
200	0.0251	0.0204	1.748	1.772
400	0.0245	0.0212	1.739	1.866
800	0.0258	0.0209	1.853	1.886
1600	0.0255	0.0205	1.824	1.836

Table CIX—Molecular Conductivity of Ammonium Bromide in Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	122.7	148.6	173.2
50	131.4	158.2	185.8
100	133.5	159.4	187.1
200	135.3	163.8	191.1
400	138.2	166.6	195.7
800	142.0	170.7	199.3
1600	147.2	172.9	205.6

Table CX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0212	0.0165	2.59	2.46
50	0.0202	0.0174	2.68	2.76
100	0.0199	0.0174	2.59	2.77
200	0.0211	0.0168	2.85	2.73
400	0.0205	0.0170	2.84	2.91
800	0.0202	0.0171	2.87	2.86
1600	0.0180	0.0183	2.57	3.27

Table CXI—Molecular Conductivity of Ammonium Bromide in a Mixture of 75 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	1.32	2.25	3.55
50	1.48	2.55	3.97
100	1.50	2.59	4.11
200	1.61	2.77	4.31
400	1.55	2.62	4.23
800	1.65	2.85	4.46
1600	1.67	2.82	4.50

Table CXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0704	0.0577	0.093	0.130
50	0.0783	0.0558	0.112	0.142
100	0.0724	0.0582	0.109	0.152
200	0.0721	0.0560	0.116	0.154
400	0.0755	0.0610	0.117	0.161
800	0.0721	0.0568	0.120	0.161
1600	0.0699	0.0591	0.115	0.168

Table CXIII—Molecular Conductivity of Ammonium Bromide in a Mixture of 50 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	3.69	5.43	7.59
50	4.30	6.28	8.77
100	4.45	6.76	9.22
200	4.68	6.90	9.72
400	4.72	7.06	9.88
800	5.02	7.48	10.45
1600	5.10	7.59	10.51

Table CXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0472	0.0397	0.174	0.216
50	0.0462	0.0396	0.198	0.249
100	0.0516	0.0369	0.231	0.246
200	0.0475	0.0401	0.222	0.282
400	0.0495	0.0399	0.234	0.282
800	0.0490	0.0393	0.246	0.297
1600	0.0489	0.0389	0.249	0.292

Table CXV—Molecular Conductivity of Ammonium Bromide in a Mixture of 25 Per cent. Glycerol with Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	8.51	10.85	13.39
50	10.54	13.94	17.37
100	11.45	14.81	18.59
200	12.50	16.23	20.41
400	12.94	16.87	21.23
800	13.92	18.12	23.07
1600	14.38	18.91	24.05

Table CXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0263	0.0237	0.234	0.254
50	0.0322	0.0247	0.340	0.343
100	0.0292	0.0255	0.336	0.378
200	0.0298	0.0259	0.373	0.418
400	0.0303	0.0258	0.393	0.436
800	0.0302	0.0273	0.420	0.495
1600	0.0314	0.0271	0.453	0.514

Table CXVII—Molecular Conductivity of Ammonium Bromide in Ethyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	16.7	19.3	21.6
50	23.8	27.3	30.9
100	26.9	31.1	35.5
200	29.8	34.7	39.8
400	34.5	40.0	47.2
800	37.6	44.2	51.0
1600	39.6	46.4	54.5

Table CXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0156	0.0119	0.260	0.230
50	0.0149	0.0130	0.350	0.360
100	0.0157	0.0137	0.420	0.440
200	0.0165	0.0144	0.490	0.510
400	0.0160	0.0180	0.550	0.720
800	0.0179	0.0154	0.660	0.680
1600	0.0178	0.0173	0.680	0.810

Table CXIX—Molecular Conductivity of Ammonium Bromide in a Mixture of 75 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	2.50	4.00	6.04
50	2.70	4.42	6.91
100	2.87	4.60	6.91
200	2.94	4.79	7.23
400	2.94	4.80	7.23
800	3.05	5.01	7.53
1600	3.06	4.99	7.62

Table CXX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0600	0.0510	0.150	0.204
50	0.0636	0.0563	0.172	0.249
100	0.0637	0.0502	0.183	0.231
200	0.0629	0.0511	0.185	0.244
400	0.0633	0.0501	0.186	0.243
800	0.0642	0.0499	0.196	0.252
1600	0.0631	0.0520	0.193	0.263

Table CXXI—Molecular Conductivity of Ammonium Bromide in a Mixture of 50 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	9.66	13.03	16.86
50	10.99	14.78	19.33
100	11.33	15.44	21.13
200	11.74	16.06	21.03
400	11.99	16.43	21.59
800	12.22	17.00	22.30
1600	12.63	17.48	22.90

Table CXXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0348	0.0293	0.337	0.383
50	0.0345	0.0308	0.379	0.455
100	0.0362	0.0368	0.411	0.569
200	0.0368	0.0308	0.432	0.497
400	0.0372	0.0314	0.444	0.516
800	0.0398	0.0311	0.478	0.530
1600	0.0383	0.0310	0.485	0.542

Table CXXIII—Molecular Conductivity of Ammonium Bromide in a Mixture of 25 Per cent. Glycerol with Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	26.0	31.4	37.3
50	30.1	36.5	43.9
100	32.4	39.4	47.0
200	33.7	41.1	49.7
400	34.9	42.5	51.1
800	36.4	44.3	53.1
1600	37.6	46.0	55.1

Table CXXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0204	0.0187	0.540	0.590
50	0.0214	0.0202	0.640	0.740
100	0.0213	0.0194	0.700	0.760
200	0.0218	0.0209	0.740	0.860
400	0.0217	0.0202	0.760	0.860
800	0.0218	0.0198	0.790	0.880
1600	0.0220	0.0193	0.840	0.910

Table CXXV—Molecular Conductivity of Ammonium Bromide in Methyl Alcohol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	59.1	65.4	73.0
50	74.2	82.9	91.7
100	79.5	90.3	99.5
200	83.3	94.1	105.7
400	89.3	98.5	111.5
800	90.9	102.2	117.3
1600	93.4	105.0	118.3

Table CXXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0107	0.0116	0.630	0.760
50	0.0116	0.0106	0.870	0.880
100	0.0136	0.0102	1.080	0.920
200	0.0130	0.0123	1.080	1.160
400	0.0103	0.0132	0.920	1.300
800	0.0125	0.0148	1.130	1.510
1600	0.0124	0.0126	1.160	1.330

Table CXXVII—Molecular Conductivity of Strontium Chloride in Glycerol at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	0.322	0.664	1.252
50	0.403	0.840	1.558
100	0.426	0.900	1.650
200	0.452	0.958	1.777
400	0.475	1.008	1.866
800	0.483	1.037	1.934
1600	0.507	1.075	1.994

Table CXXVIII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.1062	0.0885	0.0342	0.0588
50	0.1084	0.0855	0.0437	0.0718
100	0.1112	0.0833	0.0474	0.0750
200	0.1118	0.0854	0.0506	0.0819
400	0.1107	0.0851	0.0533	0.0858
800	0.1150	0.0863	0.0554	0.0897
1600	0.1101	0.0853	0.0568	0.0919

Table CXXIX—Molecular Conductivity of Strontium Chloride in a Mixture of 75 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	5.85	9.13	13.38
50	6.90	10.82	16.08
100	7.29	11.45	16.78
200	7.76	12.34	18.07
400	8.61	13.63	19.99
800	9.21	14.56	21.23
1600	9.72	15.37	22.46

Table CXXX—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0560	0.0465	0.328	0.425
50	0.0565	0.0476	0.392	0.526
100	0.0571	0.0466	0.416	0.533
200	0.0590	0.0467	0.458	0.573
400	0.0588	0.0465	0.502	0.636
800	0.0581	0.0458	0.535	0.667
1600	0.0581	0.0458	0.565	0.709

Table CXXXI—Molecular Conductivity of Strontium Chloride in a Mixture of 50 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	28.08	38.38	51.30
50	33.35	45.12	59.31
100	35.19	48.17	63.40
200	36.84	50.59	66.13
400	38.74	52.59	69.16
800	42.03	56.88	74.78
1600	42.84	59.08	79.39

Table CXXXII—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0315	0.0337	1.030	1.292
50	0.0358	0.0315	1.177	1.419
100	0.0379	0.0312	1.398	1.523
200	0.0373	0.0307	1.375	1.554
400	0.0356	0.0315	1.385	1.657
800	0.0354	0.0315	1.485	1.790
1600	0.0378	0.0343	1.624	2.031

Table CXXXIII—Molecular Conductivity of Strontium Chloride in a Mixture of 25 Per cent. Glycerol with Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	79.7	100.5	122.3
50	92.2	117.3	144.2
100	97.7	122.9	152.2
200	102.3	129.3	159.8
400	103.8	133.0	163.0
800	107.1	135.6	168.7
1600	109.2	137.3	170.2

Table CXXXIV—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0261	0.0216	2.08	2.18
50	0.0271	0.0229	2.51	2.69
100	0.0258	0.0239	2.52	2.93
200	0.0261	0.0235	2.70	3.05
400	0.0281	0.0224	2.92	3.00
800	0.0266	0.0243	2.85	3.31
1600	0.0258	0.0238	2.81	3.29

Table CXXXV—Molecular Conductivity of Strontium Chloride in Water at 25°, 35°, 45°

V	μ_v 25°	μ_v 35°	μ_v 45°
10	175.3	210.6	247.8
50	199.1	249.1	285.0
100	207.5	252.5	299.1
200	215.4	262.7	310.3
400	224.5	274.8	323.8
800	230.8	279.0	332.8
1600	235.9	285.6	342.9

Table CXXXVI—Temperature Coefficients

	Per cent.		Cond. units	
V	25°–35°	35°–45°	25°–35°	35°–45°
10	0.0201	0.0180	3.53	3.72
50	0.0250	0.0149	5.00	3.59
100	0.0214	0.0146	4.50	4.66
200	0.0219	0.0181	4.73	4.66
400	0.0224	0.0171	5.03	4.90
800	0.0209	0.0193	4.82	5.38
1600	0.0210	0.0200	4.97	5.73

Table CXXXVII—Comparison of Temperature Coefficients of Ammonium Bromide from 25° to 35° in Mixtures of Glycerol and Water

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1032	0.0536	0.0340	0.0249	0.0212
50	0.1051	0.0546	0.0341	0.0254	0.0204
100	0.1075	0.0548	0.0340	0.0255	0.0199
200	0.1080	0.0546	0.0334	0.0251	0.0211
400	0.1069	0.0553	0.0339	0.0245	0.0205
800	0.1085	0.0555	0.0342	0.0258	0.0202
1600	0.1106	0.0538	0.0325	0.0255	0.0180

Table CXXXVIII—Comparison of Temperature Coefficients of Ammonium Bromide from 25° to 35° in Mixtures of Glycerol and Ethyl Alcohol

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1032	0.0704	0.0472	0.0263	0.0156
50	0.1051	0.0783	0.0462	0.0322	0.0149
100	0.1075	0.0724	0.0516	0.0292	0.0157
200	0.1080	0.0721	0.0475	0.0298	0.0165
400	0.1069	0.0755	0.0495	0.0303	0.0160
800	0.1085	0.0721	0.0490	0.0302	0.0179
1600	0.1106	0.0699	0.0489	0.0314	0.0178

Table CXXXIX—Comparison of Temperature Coefficients of Ammonium Bromide from 25° to 35° in Mixtures of Glycerol and Methyl Alcohol

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1032	0.0600	0.0348	0.0204	0.0107
50	0.1051	0.0636	0.0345	0.0214	0.0116
100	0.1080	0.0637	0.0362	0.0213	0.0136
200	0.1075	0.0629	0.0368	0.0218	0.0130
400	0.1069	0.0633	0.0372	0.0217	0.0103
800	0.1085	0.0642	0.0398	0.0218	0.0125
1600	0.1106	0.0631	0.0383	0.0220	0.0124

Table CXL—Comparison of Temperature Coefficients of Sodium Nitrate from 25° to 35° in Mixtures of Glycerol and Water

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1033	0.0529	0.0348	0.0253	0.0198
50	0.1046	0.0561	0.0350	0.0244	0.0204
100	0.1096	0.0549	0.0352	0.0272	0.0212
200	0.1070	0.0541	0.0367	0.0267	0.0211
400	0.1058	0.0534	0.0365	0.0264	0.0190
800	0.1058	0.0538	0.0338	0.0254	0.0201
1600	0.1062	0.0531	0.0329	0.0254	0.0230

Table CXLI—Comparison of Temperature Coefficients of Sodium Nitrate from 25° to 35° in Mixtures of Glycerol and Ethyl Alcohol

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.
10	0.1033	0.0736	0.0457	0.0284
50	0.1046	0.0701	0.0470	0.0288
100	0.1070	0.0742	0.0475	0.0292
200	0.1096	0.0739	0.0478	0.0290
400	0.1058	0.0721	0.0475	0.0305
800	0.1058	0.0746	0.0478	0.0288
1600	0.1062	0.0742	0.0487	0.0305

Table CXLII—Comparison of Temperature Coefficients of Sodium Nitrate from 25° to 35° in Mixtures of Glycerol nd Methyl Alcohol

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.
10	0.1033	0.0603	0.0363	0.0214
50	0.1046	0.0652	0.0368	0.0223
100	0.1070	0.0650	0.0377	0.0224
200	0.1096	0.0714	0.0378	0.0220
400	0.1058	0.0654	0.0385	0.0225
800	0.1058	0.0613	0.0383	0.0218
1600	0.1062	0.0658	0.0390	0.0230

Table CXLIII—Comparison of Temperature Coefficients of Potassium Chloride from 25° to 35° in Mixtures of Glycerol and Water

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1006	0.0554	0.0341	0.0246	0.0188
50	0.1074	0.0556	0.0345	0.0258	0.0192
100	0.1049	0.0549	0.0336	0.0244	0.0200
200	0.1047	0.0548	0.0338	0.0253	0.0195
400	0.0948	0.0550	0.0344	0.0243	0.0201
800	0.0962	0.0553	0.0344	0.0238	0.0201
1600	0.0707	0.0558	0.0345	0.0253	0.0206

Table CXLIV—Comparison of Temperature Coefficients of Potassium Chloride from 25° to 35° in Mixtures of Glycerol and Ethyl Alcohol

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.
10	0.1006	0.0694	0.0459	0.0281
50	0.1074	0.0717	0.0471	0.0297
100	0.1049	0.0733	0.0500	0.0308
200	0.1047	0.0723	0.0451	0.0306
400	0.0948	0.0719	0.0490	0.0352
800	0.0962	0.0733	0.0491	0.0320
1600	0.0707	0.0710	0.0481	0.0319

Table CXLV—Comparison of Temperature Coefficients of Potassium Chloride from 25° to 35° in Mixtures of Glycerol and Methyl Alcohol

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.
10	0.1006	0.0612	0.0369	0.0220
50	0.1074	0.0630	0.0378	0.0218
100	0.1049	0.0640	0.0374	0.0221
200	0.1047	0.0632	0.0375	0.0230
400	0.0948	0.0625	0.0376	0.0231
800	0.0962	0.0639	0.0371	0.0227
1600	0.0707	0.0632	0.0365	0.0237

Table CXLVI—Comparison of Temperature Coefficients of Strontium Chloride from 25° to 35° in Mixtures of Glycerol and Water

V	100 per cent.	75 per cent.	50 per cent.	25 per cent.	0 per cent.
10	0.1062	0.0560	0.0315	0.0261	0.0201
50	0.1084	0.0565	0.0358	0.0271	0.0250
100	0.1112	0.0571	0.0379	0.0258	0.0214
200	0.1118	0.0590	0.0373	0.0261	0.0219
400	0.1107	0.0588	0.0356	0.0281	0.0224
800	0.1150	0.0581	0.0354	0.0266	0.0209
1600	0.1101	0.0581	0.0378	0.0258	0.0210

The last figure in all tables of "per cent." "temperature coefficients" should be disregarded.

Table CXLVII—Viscosities and Fluidities of Solutions in Glycerol at 25°, 35°, 45°

Salt	η 25°	η 35°	η 45°	θ 25°	θ 35°	θ 45°	Temp. coef. 25°–35°	Temp. coef. 35°–45°
KCl	6.362	2.836	1.399	0.1571	0.3527	0.7147	0.124	0.103
KBr	6.197	2.760	1.376	0.1613	0.3623	0.7264	0.124	0.101
KNO_3	6.065	2.734	1.353	0.1648	0.3659	0.7391	0.122	0.099
NaCl	6.716	2.920	1.445	0.1613	0.3429	0.7143	0.124	0.106
NaBr	6.439	2.865	1.400	0.1553	0.3490	0.7143	0.124	0.106
NaI	6.303	2.822	1.409	0.1586	0.3543	0.7105	0.124	0.101
$NaNO_3$	6.288	2.803	1.405	0.1590	0.3546	0.7117	0.123	0.101
NH_4Cl	6.142	2.741	1.360	0.1628	0.3649	0.7357	0.124	0.101
NH_4Br	5.970	2.681	1.329	0.1672	0.3729	0.7524	0.123	0.102
NH_4NO_3	6.306	2.800	1.408	0.1587	0.3572	0.7097	0.124	0.099
$BaCl_2$	7.447	3.288	1.626	0.1343	0.3041	0.6150	0.126	0.102
$BaBr_2$	7.100	3.199	1.571	0.1409	0.3126	0.6366	0.122	0.103
$Ba(NO_3)_2$	7.212	3.182	1.571	0.1387	0.3143	0.6516	0.126	0.107
$SrCl_2$	7.336	3.224	1.589	0.1363	0.3104	0.6291	0.127	0.103
$SrBr_2$	7.337	3.219	1.574	0.1365	0.3107	0.6354	0.127	0.104
$Sr(NO_3)_2$	7.640	3.335	1.640	0.1308	0.2998	0.6098	0.129	0.106
$CaBr_2$	7.674	3.373	1.630	0.1303	0.2964	0.6135	0.127	0.106
$Ca(NO_3)_2$	7.411	3.278	1.617	0.1350	0.3050	0.6184	0.125	0.103
Solvent	6.067	2.761	1.352	0.1648	0.3683	0.7396	0.124	0.101

Table CXLVIII—Viscosities and Fluidities of Solutions in Glycerol at 55°, 65°, 75°

Salt	η 55°	η 65°	η 75°	θ 55°	θ 65°	θ 75°	Temp. coef. 55°–65°	Temp. coef. 65°–75°
KCl	0.7435	0.4353	0.2648	1.345	2.297	3.776	0.071	0.064
KBr	0.7475	0.4353	0.2709	1.338	2.297	3.692	0.065	0.061
NaBr	0.7664	0.4439	0.2689	1.305	2.253	3.719	0.072	0.065
NH_4Cl	0.7366	0.4269	0.2613	1.357	2.342	3.827	0.072	0.063
NH_4NO_3	0.7284	0.4254	0.2618	1.373	2.351	3.819	0.071	0.062
$CoCl_2$	0.8225	0.4762	0.2884	1.215	2.099	3.467	0.073	0.065
$SrCl_2$	0.8536	0.4932	0.2984	1.172	2.028	3.355	0.073	0.065
Solvent	0.7415	0.4288	0.2620	1.350	2.331	3.817	0.072	0.063

Table CXLIX—Viscosities and Fluidities of Solutions in Glycerol at 55°, 65°, 75°

Salt	η 55°	η 65°	η 75°	θ 55°	θ 65°	θ 75°	Temp. coef. 55°–65°	Temp. coef. 65°–75°
KCl	0.6387	0.3781	0.2334	1.565	2.645	4.283	0.0689	0.0619
NH_4Cl	0.6457	0.3805	0.2318	1.548	2.628	4.313	0.0697	0.0641
NH_4NO_3	0.6251	0.3701	0.2291	1.599	2.702	4.365	0.0689	0.0616
NaI	0.6524	0.3827	0.2340	1.532	2.613	4.273	0.0705	0.0635
$Ba(NO_3)_2$	0.7080	0.4159	0.2544	1.412	2.404	3.931	0.0702	0.0635
$CoBr_2$	0.7388	0.4292	0.2638	1.353	2.329	3.789	0.0721	0.0629
Solvent	0.6370	0.3732	0.2309	1.569	2.678	4.329	0.0706	0.0616

Table CL—Viscosities and Fluidities of Solutions in Mixtures of Glycerol with Water at 25°, 35°, 45°

In Glycerol

Salt	η 25°	η 35°	η 45°	θ 25°	θ 35°	θ 45°	Temp. coef. 25°–35°	Temp. coef. 35°–45°
KCl	6.362	2.836	1.399	0.1571	0.3527	0.7147	0.124	0.103
NH_4Br	5.970	2.681	1.329	0.1672	0.3729	0.7524	0.123	0.102
$NaNO_3$	6.288	2.803	1.405	0.1590	0.3546	0.7117	0.123	0.101
$SrCl_2$	7.336	3.224	1.589	0.1363	0.3104	0.6291	0.127	0.103
Solvent	6.067	2.761	1.352	0.1648	0.3683	0.7396	0.124	0.101

In 75 Per cent. Glycerol with Water

KCl	0.3394	0.2003	0.1293	2.943	4.993	7.733	0.0698	0.0549
NH_4Br	0.3278	0.1932	0.1249	3.035	5.176	8.008	0.0699	0.0547
$NaNO_3$	0.3274	0.1947	0.1233	3.054	5.137	8.111	0.0682	0.0558
$SrCl_2$	0.3642	0.2179	0.1326	2.746	4.696	7.543	0.0713	0.0606
Solvent	0.3169	0.1884	0.1186	3.156	5.307	8.431	0.0681	0.0586

In 50 Per cent. Glycerol with Water

KCl	0.06481	0.04385	0.03187	15.27	22.82	31.37	0.0422	0.0347
NH_4Br	0.06085	0.04251	0.03102	16.43	23.52	32.05	0.0431	0.0321
$NaNO_3$	0.06333	0.04372	0.03216	15.79	22.87	31.10	0.0447	0.0363
$SrCl_2$	0.06607	0.04563	0.03335	15.13	21.90	29.99	0.0379	0.0369
Solvent	0.06109	0.04233	0.03114	16.37	23.63	32.10	0.0438	0.0358

In 25 Per cent. Glycerol with Water

KCl	0.02054	0.01546	0.01246	48.68	64.67	80.25	0.0328	0.0242
NH_4Br	0.02046	0.01552	0.01226	48.88	64.50	81.56	0.0320	0.0264
$NaNO_3$	0.02086	0.01556	0.01235	47.95	64.28	80.96	0.0340	0.0245
$SrCl_2$	0.02145	0.01614	0.01277	46.62	61.97	78.31	0.0329	0.0263
Solvent	0.01946	0.01466	0.01171	51.38	68.22	85.45	0.0327	0.0253

In Water

KCl	0.00902	0.00729	0.00608	110.8	137.0	164.6	0.0243	0.0201
NH_4Br	0.00894	0.00722	0.00609	112.0	138.6	164.1	0.0246	0.0199
$NaNO_3$	0.00903	0.00732	0.00608	110.8	136.6	164.4	0.0236	0.0202
$SrCl_2$	0.00927	0.00749	0.00628	107.9	133.5	159.4	0.0237	0.0194
Solvent	0.00891	0.00720	0.00598	112.2	138.9	167.2	0.0237	0.0204

Table CLI—Viscosities and Fluidities of Solutions in Mixtures of Glycerol with Ethyl Alcohol at 25°, 35°, 45°

In 75 Per cent. Glycerol with Ethyl Alcohol

							Temp. coef.	
Salt	25°	35°	45°	25°	35°	45°	25°–35°	35°–45°
KCl	1.123	0.5942	0.3387	0.8904	1.683	2.952	0.0890	0.0754
NH_4Br	1.085	0.5762	0.3291	0.9214	1.736	3.039	0.0885	0.0751
$NaNO_3$	1.171	0.6185	0.3509	0.8547	1.635	2.850	0.0900	0.0762
Solvent	1.029	0.5404	0.3111	0.9720	1.830	3.215	0.0912	0.0759

In 50 Per cent. Glycerol with Ethyl Alcohol

KCl	0.2175	0.1377	0.08840	4.598	7.381	11.31	0.0605	0.0533
NH_4Br	0.2163	0.1325	0.08668	4.731	7.550	11.54	0.0595	0.0528
$NaNO_3$	0.2213	0.1360	0.08906	4.523	7.353	11.23	0.0620	0.0527
Solvent	0.2123	0.1351	0.08723	4.712	7.402	11.46	0.0600	0.0529

In 25 Per cent. Glycerol with Ethyl Alcohol

KCl	0.04473	0.03263	0.02487	22.36	30.66	40.21	0.0371	0.0311
NH_4Br	0.04396	0.03227	0.02442	22.75	31.01	40.94	0.0369	0.0326
$NaNO_3$	0.04464	0.03276	0.02481	22.40	30.52	40.31	0.0362	0.0320
Solvent	0.04184	0.03061	0.02303	23.90	32.77	43.42	0.0371	0.0324

In Ethyl Alcohol

NH_4Br	0.01216	0.009526	0.007979	86.13	105.1	125.3	0.0219	0.0193
Solvent	0.01068	0.008683	0.007292	93.70	115.2	137.7	0.0227	0.0191

Table CLII—Viscosities and Fluidities of Solutions in Mixtures of Glycerol with Methyl Alcohol at 25°, 35°, 45°

Salt	25°	35°	45°	25°	35°	45°	Temp. coef. 25°–35°	Temp. coef. 35°–45°
In 75 Per cent. Glycerol with Methyl Alcohol								
KCl	0.6308	0.3512	0.2129	1.585	2.850	4.696	0.0797	0.0659
NH_4Br	0.5999	0.3347	0.2011	1.666	2.987	4.973	0.0793	0.0665
$NaNO_3$	0.6362	0.3590	0.2122	1.572	2.786	4.713	0.0771	0.0689
Solvent	0.6242	0.3519	0.2087	1.609	2.842	4.792	0.0763	0.0681
In 50 Per cent. Glycerol with Methyl Alcohol								
KCl	0.09521	0.06367	0.04474	10.51	15.70	22.35	0.0494	0.0423
NH_4Br	0.09225	0.06300	0.04361	10.84	15.87	22.93	0.0464	0.0444
$NaNO_3$	0.09717	0.06502	0.04574	10.29	15.74	21.87	0.0496	0.0436
Solvent	0.09657	0.06512	0.04446	10.35	15.35	22.50	0.0484	0.0468
In 25 Per cent. Glycerol with Methyl Alcohol								
KCl	0.02083	0.01631	0.0131	48.02	61.32	76.31	0.0276	0.0244
NH_4Br	0.02064	0.01610	0.0130	48.46	62.11	76.01	0.0261	0.0223
$NaNO_3$	0.02098	0.01627	0.0130	47.75	61.48	76.46	0.0287	0.0243
Solvent	0.01886	0.01481	0.0119	53.01	67.53	83.71	0.0274	0.0240
In Methyl Alcohol								
NH_4Br	0.006254	0.005410	0.004745	159.9	184.8	211.2	0.0155	0.0143
Solvent	0.005842	0.005066	0.004469	171.2	197.4	223.7	0.0157	0.0139

Table CLIII—Table Showing Viscosities and Fluidities of Substances which were Found to Lower the Viscosity of Pure Glycerol at 25°, 35°, and 45°

Salt	V	25°	35°	45°	25°	35°	45°	Temp. coef. 25°–35°	Temp. coef. 35°–45°.
$NaNO_3$	0.10	5.367	2.425	1.222	0.1863	0.4125	0.8186	0.121	0.100
NH_4Br	0.10	5.206	2.329	1.187	0.1929	0.4264	0.8423	0.121	0.098
NH_4Br	0.50	5.071	2.324	1.189	0.1972	0.4302	0.8409	0.118	0.096
NH_4I	0.10	5.108	2.320	1.165	0.1957	0.4308	0.8583	0.118	0.098
NH_4I	0.50	4.605	2.157	1.080	0.2173	0.4745	0.9259	0.118	0.096
RbBr	0.10	5.183	2.332	1.176	0.1975	0.4288	0.8502	0.117	0.098
RbBr	0.50	4.768	2.183	1.112	0.2098	0.4583	0.8998	0.118	0.096
Solvent	..	5.298	2.366	1.198	0.1888	0.4226	0.8347	0.118	0.097

DISCUSSION OF RESULTS

A rise in temperature causes an increase in conductivity, which may be due to either or to both of the following causes: First, an increase in the number of the ions present, and second, an increase in the velocity of the ions. That the number of the ions does not generally increase with rise in temperature has been shown by direct measurement of the degree of dissociation by means of the conductivity method. This is in accord with the theory of Dutoit and Aston,[1] which

[1] *Loc. cit.*

makes the dissociating power of a solvent a function of its own association. The degree of association of a solvent has been shown by the method of Ramsay and Shields[1] to decrease with rise in temperature; hence, its power to dissociate an electrolyte into its ions has been diminished. It is, however, true that the theory of Dutoit and Aston is only an approximation.

The increase in velocity of the ions with rise in temperature must then be the one conditioning cause of the increase in conductivity. This change in velocity of the ions may be due to either or to both of the following causes: First, change in the viscosity of the medium through which the ions move; second, as Jones[2] and his coworkers have shown, to the change in complexity of the solvates which surround the ion.

In no other solvent is the change in conductivity with change in temperature so pronounced as in the one which chiefly concerns this investigation, viz., glycerol. The chief cause of this change is largely the change in the viscosity of the solution, while we believe that there is some evidence brought out in this investigation that indicates the presence of glycerolates.

Tables I to XXXVI, inclusive, give the molecular conductivities at 25°, 35° and 45° of all the electrolytes which we have studied in pure glycerol as a solvent. It is seen that in all cases the values for μ_v are extremely small, but show, in general, a regular increase, both with increased dilution and with rise in temperature.

Associated with each table of conductivity is a table giving the temperature coefficients of conductivity, both in per cent. and in conductivity units. Since the latter show the actual increase in conductivity per degree rise in temperature, a discussion of these data will bring out the most interesting points of this part of the work.

Although the temperature coefficients of conductivity, when expressed in conductivity units, show, in general, a regular increase with increased dilution, yet this is much

[1] *Loc. cit.*

[2] THIS JOURNAL, **35**, 445 (1906).

more marked with ternary than with binary electrolytes. This fact has been observed by Jones[1] for aqueous solutions in a discussion of the work of West.[2]

Results of the present investigation show that in glycerol the temperature coefficients of conductivity of any given substance, at high dilution, are larger than at lower dilution, and that the relative increase is greater with salts of barium, strontium, calcium, and cobalt than with salts of sodium, potassium and ammonium. These facts may be explained in terms of the theory of solvation. That solvation takes place in aqueous solution has been shown beyond reasonable doubt by Jones and his coworkers; and, indeed, Jones and Strong have obtained abundant spectroscopic evidence for solvates in glycerol as a solvent.

If there is solvation, then, according to the mass law, in the more dilute solutions, where the amount of solvate per ion is greatest, we should expect to find the most complex solvates. Any change in temperature would produce the greatest effect where the solvation was greatest, that is, in the most dilute solutions. Again, this change in solvation should be more apparent in those salts which have the greater power of combining with the solvent, or, in the case of water, with those salts that have the largest number of molecules of water of crystallization.

We cannot, of course, say that salts of barium, strontium, calcium, and cobalt possess a power of combining with glycerol similar to that which they manifest towards water, but it is not surprising to find solvation more marked with these salts than with salts that have very slight hydrating power, such as the salts of sodium, potassium and ammonium.

It is also true that salts of approximately the same hydrating power show, in glycerol, temperature coefficients of the same order of magnitude.

The molecular conductivities at low dilutions in nearly every case are smaller for ternary than for binary electrolytes, while at higher dilutions the reverse is true without excep-

[1] *Loc. cit.*

[2] THIS JOURNAL, **34**, 357 (1905).

tion. This may be due to the fact that glycerol is only a fair dissociating agent, resembling methyl and ethyl alcohols, and has, at moderate concentrations, the power of producing only two ions from a ternary electrolyte, or at least dissociating a ternary electrolyte only to a moderate extent.

We should expect to find the ternary electrolytes yielding more ions at higher dilutions, and, hence, showing a greater molecular conductivity than binary electrolytes under the same conditions. That this is true may be best shown by comparing the molecular conductivities of several of the binary and ternary electrolytes used.

Salt	μ_v 10	μ_v 1600
KNO_3	0.337	0.431
KBr	0.366	0.413
NaCl	0.328	0.395
$BaBr_2$	0.330	0.530
$Ba(NO_3)_2$	0.246	0.462
$Ca(NO_3)_2$	0.283	0.472
$SrCl_2$	0.322	0.507

In the above table the molecular conductivities of several typical salts at 25° are compared at volumes 10 and 1600, respectively. These data confirm the above statement, that while at low dilutions a ternary electrolyte usually has the smaller molecular conductivity, at higher dilutions the reverse is usually true.

Tables XXXVII to LVI give the molecular conductivities and temperature coefficients of conductivity of all the salts studied at 55°, 65° and 75°. The same general relations hold at these temperatures as at the lower temperatures, viz., a regular increase in conductivity with increased dilution and rise in temperature; and a more marked increase, or a larger temperature coefficient, with those salts which in aqueous solutions possess the greatest power of hydration. The same reasoning employed above for the lower temperatures is applicable here.

Tables LVII to CXXXVI, inclusive, contain the data for the molecular conductivity and temperature coefficients of conductivity, expressed both in per cent. and in conductivity units,

for potassium chloride, sodium nitrate, ammonium bromide, and strontium chloride in the various mixtures of glycerol with water, methyl alcohol, and ethyl alcohol. The results are plotted in Figures I to X, inclusive.

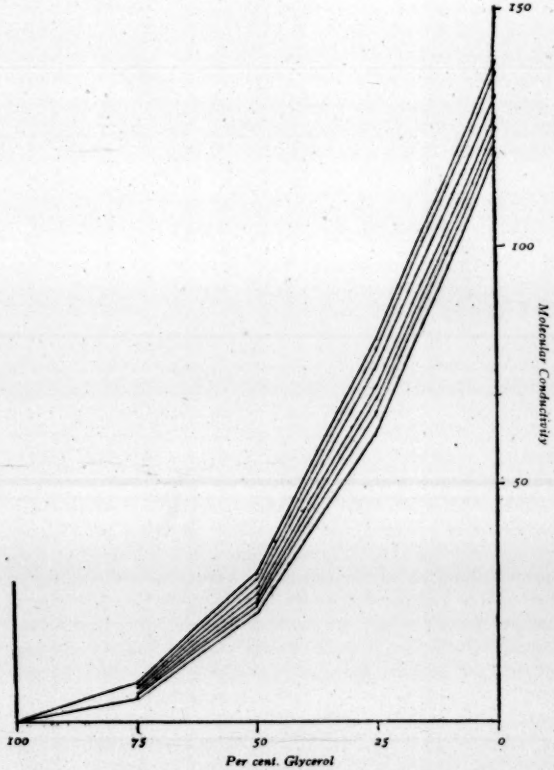

Fig. I—Conductivity of Potassium Chloride in Glycerol-Water at 25°

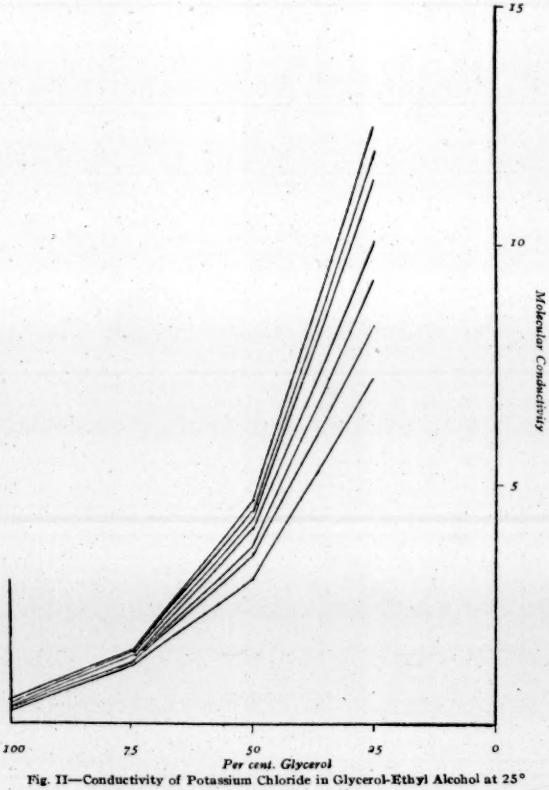

Fig. II—Conductivity of Potassium Chloride in Glycerol-Ethyl Alcohol at 25°

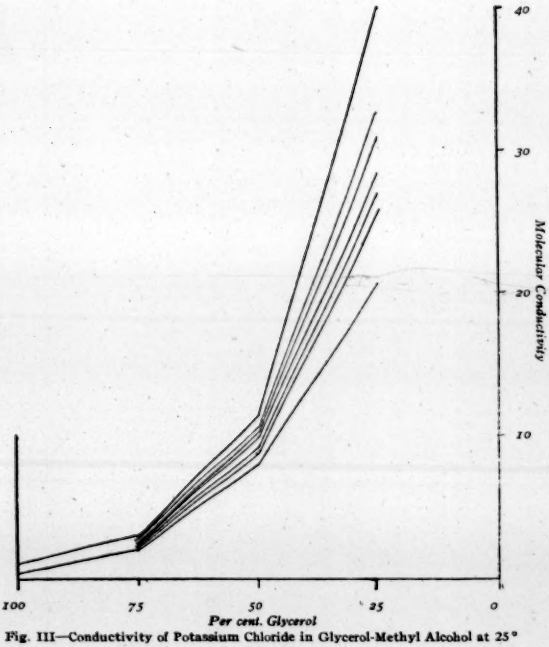

Fig. III—Conductivity of Potassium Chloride in Glycerol-Methyl Alcohol at 25°

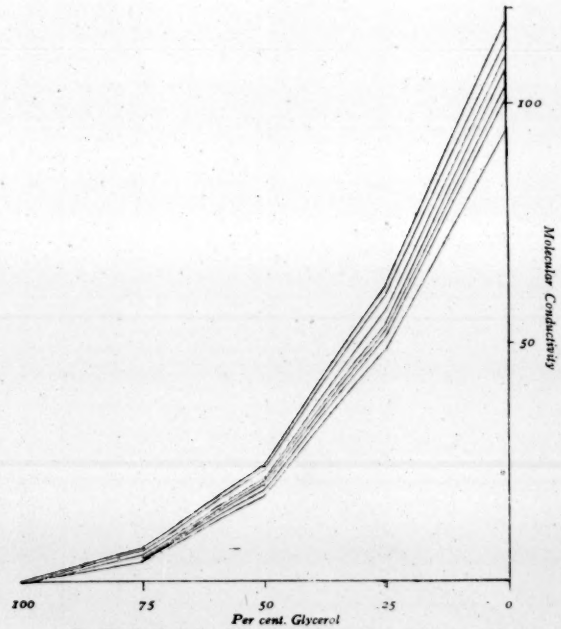

Fig. IV—Conductivity of Sodium Nitrate in Glycerol-Water at 25°

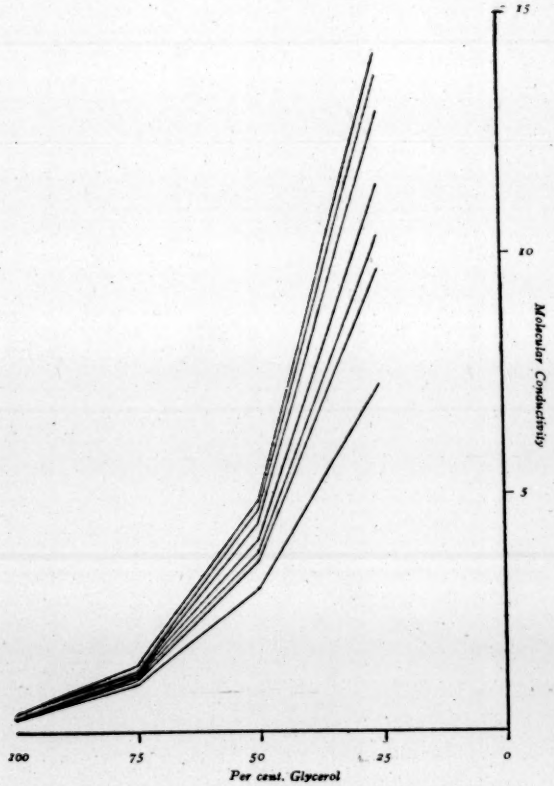

Fig. V—Conductivity of Sodium Nitrate in Glycerol-Ethyl Alcohol at 25°

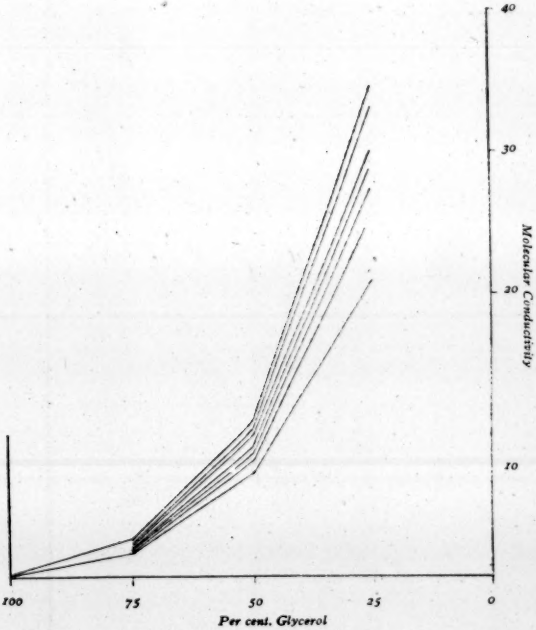

Fig. VI—Conductivity of Sodium Nitrate in Glycerol-Methyl Alcohol at 25°

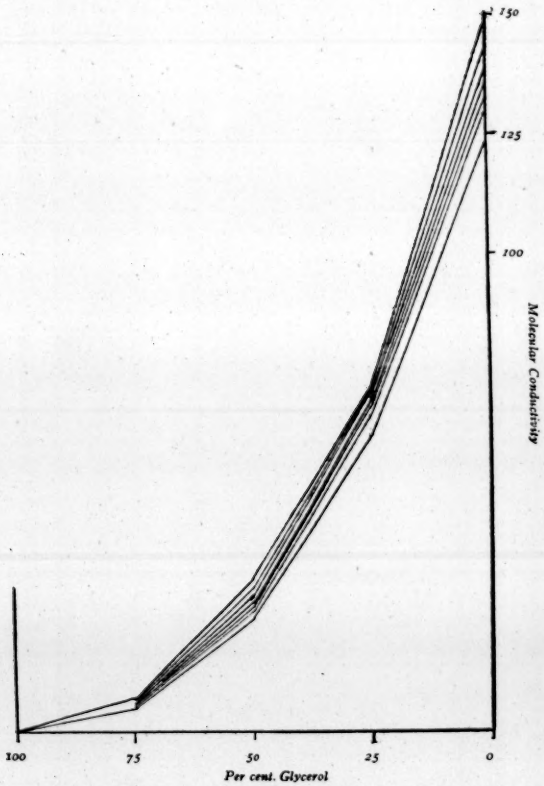

Fig. VII—Conductivity of Ammonium Bromide in Glycerol-Water at 25°

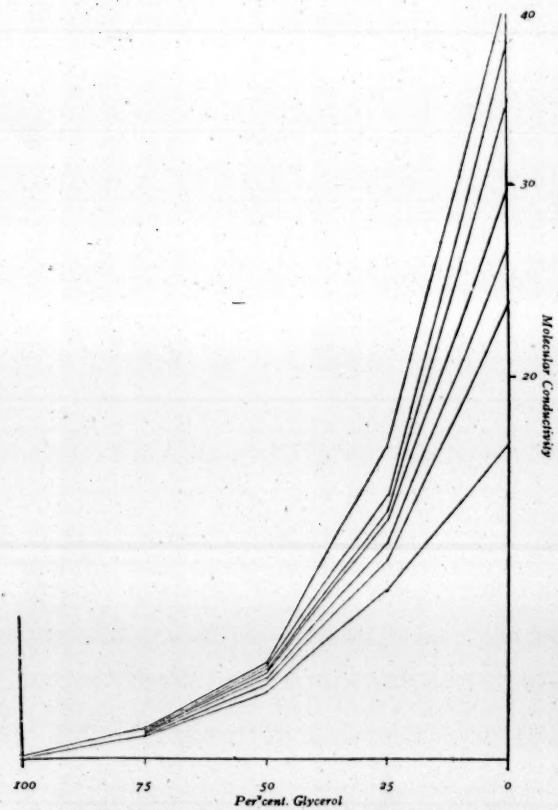

Fig. VIII—Conductivity of Ammonium Bromide in Glycerol-Ethyl Alcohol at 25°

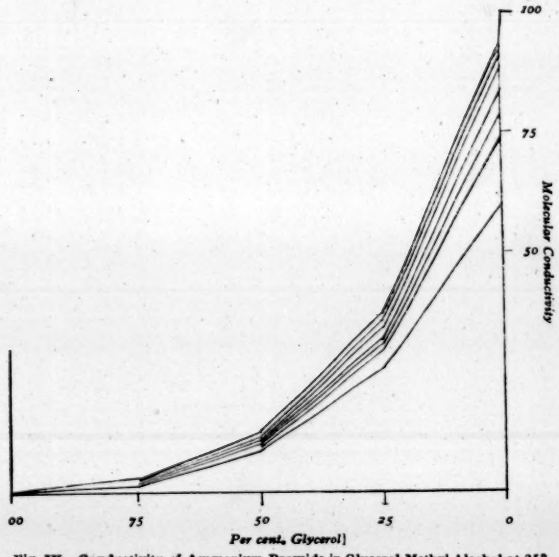

Fig. IX—Conductivity of Ammonium Bromide in Glycerol-Methyl Alcohol at 25°

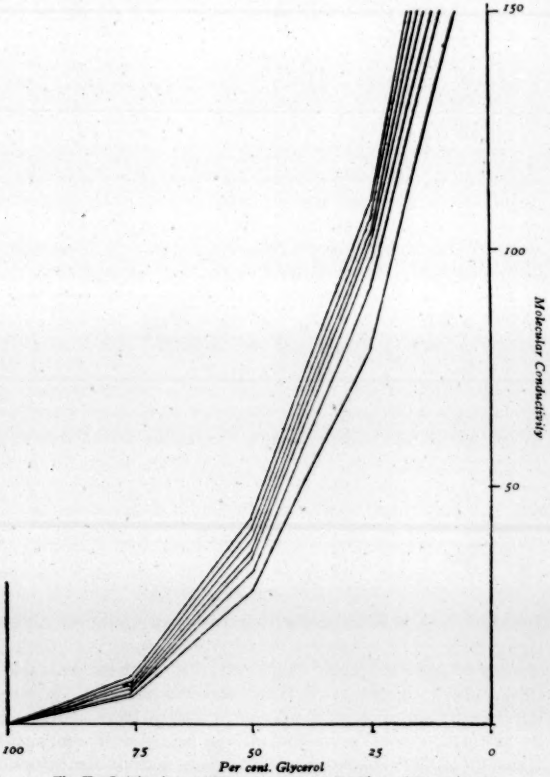

Fig. X—Conductivity of Strontium Chloride in Glycerol-Water at 25°

These curves show that the conductivities in such mixtures do not follow the law of averages, but are always less. In every case there is a marked sagging of the curves, but in no instance was a minimum obtained. This deviation from the law of averages has been explained by the work of Jones with Lindsay and Murray, which has been discussed elsewhere in this paper. When glycerol is mixed with water, or with either of the alcohols, it is clear that the properties of the mixture are not additive, the one solvent tending to lessen the association of the other; and, hence, their combined power of dissociating electrolytes is less than would be expected if there were no such lowering of each other's association.

Potassium chloride and sodium nitrate are nearly insoluble in the alcohols, and yet curves expressing the conductivities of these salts in mixtures of the alcohols with glycerol are strikingly similar to those of ammonium bromide. This seems to indicate that the deviation from the law of averages is due largely to the change in association of the glycerol.

Tables CXXXVII to CXLVI, inclusive, give a comparison of the percentage temperature coefficients of conductivity from 25° to 35° of all the salts we have studied in mixed solvents. In pure glycerol these values are very large, being from ten to eleven per cent. per degree rise in temperature. They decrease very rapidly with the addition of either water or the alcohols. The temperature coefficients also decrease very rapidly with rise in temperature.

VISCOSITIES AND FLUIDITIES

Table CXLVII includes the viscosities and fluidities of the eighteen electrolytes whose conductivities we have studied. Measurements were made only with the tenth-normal solutions, since, at higher dilutions, the difference in viscosity between the solution and solvent is hardly large enough to be detected, much less measured. In nearly every case the viscosity of the solution is greater than that of the solvent. Ammonium bromide was found to be an exception to this rule, and will be discussed more fully. The temperature coefficients of fluidity are very large and almost equal to the

temperature coefficients of conductivity. That the former are larger than the latter is not surprising, since rise in temperature would decrease the dissociation and thus decrease the conductivity, which would, at least in part, offset the increase in conductivity caused by increase in fluidity.

The ternary electrolytes show a much greater increase in viscosity than the binary electrolytes. It will be recalled that the salts which show the greatest increase in viscosity are those in which the solvation seemed to be the greatest.

This increase in viscosity of the ternary over the binary electrolytes may be due to several causes. There may be a greater number of ions present, which, since the viscosity is a function of the skin friction, would increase the viscosity; or the molecules of the solvent, combined as solvates, may be so attached to the molecule of the solute as to hinder its movement. It is not supposed that in any case of solvation the molecules of the solvent are so held as to form a complex chemical molecule, since this would, of course, decrease the skin friction and thus lessen the viscosity of the solution.

The fact that solutions of ternary electrolytes show greater viscosities than solutions of binary electrolytes may be a conditioning factor in the small molecular conductivity shown by them in the more concentrated solutions. It is, however, hardly possible that this could account entirely for the phenomenon, since there is probably less actual dissociation of a ternary than of a binary electrolyte in the most concentrated solutions.

It is probable, then, that the large viscosity of the ternary electrolytes in glycerol is due to a summation of at least two effects: The small atomic volumes of barium, strontium, calcium and cobalt, and possibly to some factor caused by solvation of the ions or molecules of the electrolytes, which, as stated above, would probably be greater with the salts of these metals than with salts of sodium, potassium and ammonium.

Tables CXLVIII and CXLIX give the corresponding viscosity data at 55°, 65° and 75°. The same general relations seem to hold at the higher as at the lower temperatures. It was found necessary to give these results in two tables, since

the specific viscosity of the two samples of glycerol used in this part of the work differed to some extent. There was only a small difference in the specific conductivity of the two specimens used. This difference in viscosity may be due to some polymerization of the glycerol. The temperature coefficients of fluidity at these higher temperatures are very similar to those of conductivity at the same temperatures.

From the data obtained, we are justified in concluding that curves representing change in conductivity and change in fluidity with rise in temperature are very similar to one another. In a word, conductivity seems to follow fluidity quite closely over the range of temperature from 25° to 75°.

The fact that glycerol has such a very large temperature coefficient of viscosity presents the possibility of throwing some light upon the relation between viscosity and reaction velocity. It has long been felt that the viscosity of the medium in which the reaction is taking place must be taken into consideration, and if the velocity of some reaction could be followed, using glycerol as a solvent, it is highly probable that interesting results would be obtained. Glycerol, being such an excellent solvent, seems well adapted to such work.

The viscosities and fluidities of solutions in the various mixtures of glycerol with the alcohols and with water are given in Tables CL to CLII, inclusive. Measurements were made only with the tenth-normal solutions, since the viscosities of the more dilute solutions differ very slightly from that of the solvent in each case. Curves representing the change in fluidity with concentration of glycerol are given in Figure XI. These curves are, in general, strikingly analogous to the curves representing the conductivities in the same mixtures, though it is seen that the increase in fluidity is more rapid than the increase in conductivity. The viscosities of the solutions are in nearly every case greater than that of the pure solvent.

NEGATIVE VISCOSITY COEFFICIENTS

One of the most interesting points brought out in this investigation is the fact that *certain salts have been found to*

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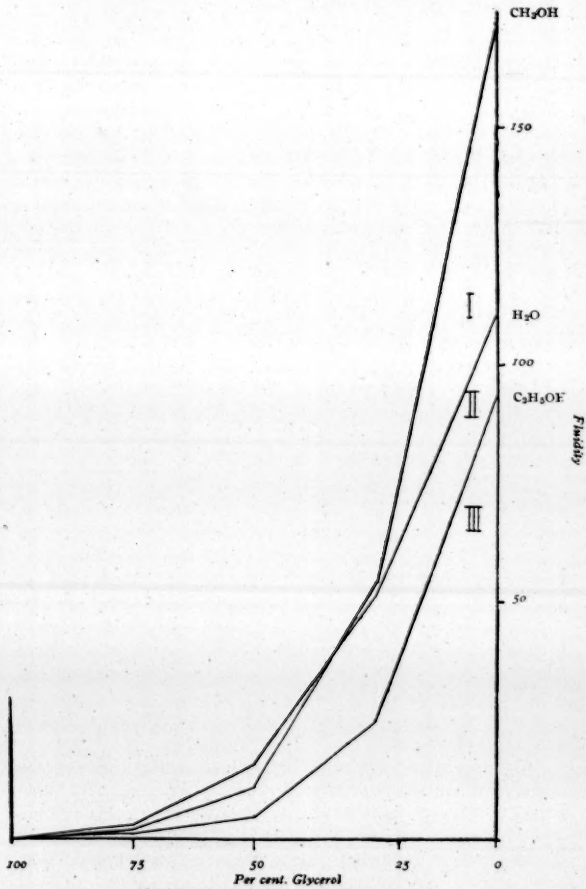


Fig. XI—Fluidity of Glycerol Mixtures at 25°

lower the viscosity of glycerol. The fact that certain electrolytes have the power to lower the viscosity of water has been known for some time, and the various theories put forward to explain such phenomena have been discussed elsewhere in this paper. Jones and Veazey[1] were the first to offer an apparently satisfactory explanation, the large atomic volumes of the metals whose salts produced such a change being the key to the phenomenon. The presence of elements with large atomic volumes, as has been stated, would decrease the amount of skin friction in a given volume of solution, and, thus, in terms of the theory of Thorpe and Rodger, would decrease the viscosity. Jones and Veazey pointed out that only salts of potassium, rubidium, and caesium produce a decrease in the viscosity of water, and that these salts do so in a direct ratio to their respective atomic volumes. Schmidt[1] had noted that the increase in viscosity of solutions in glycerol over that of the pure solvent was in an inverse ratio to the atomic volumes of the metals whose salts he studied; but in no case did he find a negative viscosity coefficient in pure glycerol.

The results showing negative viscosities in glycerol are given in Table CLIII. From this table it can be seen that one-tenth gram-molecule of rubidium bromide lowers the viscosity of glycerol about two per cent., while one-half gram-molecule lowers the viscosity of the solvent over eight per cent.

This lowering of the viscosity of glycerol by a salt of rubidium is analogous to the lowering of the viscosity of water produced by the same salt. The explanation of this phenomenon may be sought for in the theory of Jones and Veazey, as elaborated in the introduction to this paper, i. e., the large atomic volume of rubidium.

Ammonium bromide and ammonium iodide produce the same effect on the viscosity of glycerol, as is seen in Table CLIII. It is clear that we can not speak of the atomic volume of ammonium, since we know of it neither in the "atomic" nor the "free" condition. It is, however, well known that

[1] *Loc. cit.*

ammonium is closely analogous chemically to potassium, caesium and rubidium, and it is not surprising to find it exhibiting the same physical behavior, such as the effect on the viscosity of a solvent.

Summary of Conclusions Drawn from this Investigation

(1) Glycerol forms mixtures with water, ethyl alcohol, and methyl alcohol whose properties are not additive. This is in agreement with the work of Jones and Schmidt.

(2) Curves representing fluidity and conductivity are very similar to one another over the range of temperature from 25° to 75°.

(3) Salts which have the highest power of solvation show the greatest temperature coefficients of conductivity, and these are greater in the more dilute solutions.

(4) In mixed solvents containing glycerol, with water, ethyl and methyl alcohols, the curves representing conductivity and fluidity are strikingly analogous.

(5) The molecular conductivities of ternary electrolytes in glycerol at low dilutions are usually smaller than those of binary electrolytes under the same conditions, while at high dilutions the reverse is generally true.

(6) While the majority of the salts studied increase the viscosity of glycerol, yet certain salts of rubidium and ammonium *lower the viscosity of glycerol.*

(7) Some evidence for the existence of glycerolates has been given.

Work in glycerol as a solvent is now being continued in this laboratory by two investigators and we intend to study very thoroughly the physical chemistry of this solvent.

JOHNS HOPKINS UNIVERSITY,
MAY, 1911.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND CINNAMYLIDENE ESTERS

III. REACTIONS WITH THE ISOMERIC METHYL ESTERS OF CINNAMYLIDENACETIC ACID[1]

By Grace Potter Reynolds

In continuing the investigation of cinnamylidene esters for the purpose of determining the influence of the second ethylene linkage on the system C : C.C : O, the next ester in the series to be studied was methyl cinnamylidenacetate. The addition reactions previously investigated with esters of substituted cinnamylidenacetic acids show that the character of the products formed is determined by the substituent in the α-position to the carboxyl group. Methyl cinnamylidenemalonate[2] and ethyl α-cyancinnamylidenacetate[3] react readily with both aromatic and aliphatic magnesium compounds, giving only 1,4-addition products, the strongly negative carboxyl and cyanogen groups in the α-position preventing the replacement of the alkoxyl group of the esters. The addition of the Grignard reagent to the methyl ester of α-phenylcinnamylidenacetic acid,[4] however, takes place only in boiling ether and the product in this case is not an ester formed by 1,4-addition but a ketone or tertiary alcohol formed by replacement of the alkoxyl group and subsequent addition, either 1,2 or 1,4, to the product first formed.

In the study of the esters of cinnamylidenacetic acid described in this paper complications were anticipated because of the presence in the esters of a mobile hydrogen atom in the α-position to the carboxymethyl group. With both aromatic and aliphatic magnesium compounds, complex substances were formed which interfered to a great extent with the isolation of the primary products of the reactions. By using a large excess of the Grignard product and keeping the re-

[1] Second paper. Reimer and Reynolds: This Journal, **40**, 428.
[2] Reimer: *Ibid.*, **38**, 227.
[3] Macleod: *Ibid.*, **44**, 331.
[4] Reimer and Reynolds: *Loc. cit.*

action mixture at a very low temperature, however, a minimum yield of complex product was obtained.

The isomeric esters react readily at —10° with phenylmagnesium bromide; the final product in both cases is the same substance, formed by replacement of alkoxyl with phenyl and subsequent 1,4-addition to the ketone first formed. The behavior of the two esters, however, is not identical. Examination of the products obtained when equal quantities of the two esters were allowed to react under exactly similar conditions with phenylmagnesium bromide indicated that the esters show a difference in the ease with which the reaction takes place. From the products obtained with the ester of the stable acid one-third of the original ester was recovered unchanged, whereas all the ester of the allo acid had reacted.

The course of these reactions may be compared with that of α-phenylcinnamylidenacetic acid ester and phenylmagnesium bromide:

$$C_6H_5CH : CHCH : CHCOOCH_3 + C_6H_5MgBr \longrightarrow [C_6H_5CH : CHCH : CHCOC_6H_5]$$

$$[C_6H_5CH : CHCH : CHCOC_6H_5] + C_6H_5MgBr \longrightarrow C_6H_5CH : CHCH(C_6H_5)CH_2COC_6H_5$$

$$C_6H_5CH : CHCH : \underset{(C_6H_5)}{C}COOCH_3 + C_6H_5MgBr \longrightarrow [C_6H_5CH : CHCH : C(C_6H_5)COC_6H_5]$$

$$[C_6H_5CH : CHCH : C(C_6H_5)COC_6H_5] + C_6H_5MgBr \longrightarrow C_6H_5CH : CHCH(C_6H_5)CH(C_6H_5)COC_6H_5$$

The character of the product formed is the same, as might be expected, since the cinnamylidenacetic acid ester differs from the α-phenyl acid ester only in that it has the more strongly positive hydrogen atom in the α-position in place of a phenyl group.

The reaction between the ester of the stable acid and ethylmagnesium bromide takes place very violently even at —15°; the sole primary product is a tertiary alcohol formed by replacement of methoxyl with ethyl and subsequent 1,2-addition of ethylmagnesium bromide to the resulting ethyl ketone.

From the reaction between the ester of the stable acid and benzylmagnesium bromide three primary products were isolated. Their formation may be expressed thus:

$$C_6H_5CH:CHCH:CHCOOCH_3 + C_6H_5CH_2MgBr \longrightarrow [C_6H_5CH:CHCH:CHCOCH_2C_6H_5]$$

This unsaturated ketone at once reacts with benzylmagnesium bromide to form both 1,2- and 1,4-addition products:

$$[C_6H_5CH:CHCH:CHCOCH_2C_6H_5] + C_6H_5CH_2MgBr \longrightarrow C_6H_5CH:CHCH:CHC(CH_2C_6H_5)(OH)CH_2C_6H_5$$

$$[C_6H_5CH:CHCH:CHCOCH_2C_6H_5] + C_6H_5CH_2MgBr \longrightarrow C_6H_5CH:CHCH(CH_2C_6H_5)CH_2COCH_2C_6H_5$$

The third product is an ester formed by 1,4-addition to the original ester:

$$C_6H_5CH:CHCH:CHCOOCH_3 + C_6H_5CH_2MgBr \longrightarrow C_6H_5CH:CHCH(CH_2C_6H_5)CH_2COOCH_3$$

When 1,4-addition was established in this case, the reactions with both phenylmagnesium bromide and ethylmagnesium bromide were repeated with greatest care in an attempt to find any trace of 1,4-addition product that might have been lost in earlier experiments. If any 1,4-ester was formed in either case, it could not be isolated by the method of separation adopted.

EXPERIMENTAL

For the preparation of the large quantities of cinnamylidenacetic acid needed in this work, the Doebner method,[1] as modified by Hinrichsen,[2] was first used, but was abandoned because a poor yield of cinnamylidenacetic acid was invariably obtained. The method of Liebermann[3] was adopted; it was found possible, however, to carry out the reaction with much larger quantities of material than were recommended by Liebermann. The procedure was as follows: To 64 grams

[1] Ber. d. chem. Ges., **33**, 2140.
[2] Ann. Chem. (Liebig), **336**, 197.
[3] Ber. d. chem. Ges., **28**, 1441.

of quinoline in a tall beaker 100 grams of cinnamylidenemalonic acid[1] were added quickly and with vigorous stirring. When the quinoline salt had formed, the beaker was heated at 170° in an oil bath for about half an hour until evolution of carbon dioxide ceased. The oily product was poured, while still warm, into iced hydrochloric acid; the crude acid separated in the solid condition on standing. It was dissolved in sodium carbonate and the sodium salt of cinnamylidenacetic acid was purified by extracting the solution with ether. The acid was precipitated from a dilute solution of the purified salt. When the slightly yellow product was recrystallized from benzene, the first crop of crystals was the allo acid; the mother liquor contained a mixture of the allo and stable acids. A 50 per cent. yield of pure acids was obtained. After several recrystallizations from benzene both of the isomers were absolutely colorless.

The stable acid used for the preparation of the ester was obtained by the isomerization of the allo acid in the sunlight. The mixture of the two isomers invariably obtained in the preparation of the allo acid was also used for this reaction. It was found very difficult to separate the stable acid in the pure condition, however, if the large quantity of iodine recommended by Liebermann was used for the isomerization, but the acid could be separated easily in pure condition by using a small quantity of iodine as catalyst. Accordingly, for the reaction, 22 grams of pure allo acid were dissolved in 275 cc. of benzene, to which 0.25 gram of iodine was added. Isomerization took place almost instantaneously in the bright sunlight; the trace of iodine was volatilized during the process of filtering the acid.

The ester of the allo acid was prepared by heating the acid on a water bath for one hour with 4 parts by weight of a 3 per cent. solution of hydrochloric acid in methyl alcohol. The oily product was poured into iced sodium carbonate, the solution extracted with ether and the ethereal extract carefully dried over calcium chloride. The lemon-yellow liquid

[1] Ber. d. chem. Ges., **28**, 1439. Ann. Chem. (Liebig), **306**, 252.

left after removal of the ether was used without further purification.

Analysis:

0.1661 gram substance gave 0.4666 gram CO_2 and 0.1015 gram H_2O.

	Calculated for $C_{12}H_{12}O_2$	Found
C	76.59	76.61
H	6.38	6.78

The ester is a liquid at ordinary temperature, and solidifies at about —15° to a white crystalline mass. It is partially changed into the ester of the stable acid by distillation under diminished pressure.

The ester of the stable acid was prepared by heating the acid on a water bath for 1.5 hours with 6 parts, by weight, of a 3 per cent. solution of hydrochloric acid in methyl alcohol. On cooling, the alcohol solution deposited a quantitative yield of solid ester.

Since both of the esters of cinnamylidenacetic acid decompose on standing, in the Grignard reaction with the ester of the allo acid it was necessary to use freshly prepared material; and the ester of the stable acid was always redistilled or recrystallized before adding it to the organic magnesium compounds.

The first reactions between the esters and the Grignard reagent were carried out in an atmosphere of carefully dried hydrogen. Subsequent work, however, showed that this extreme precaution was not necessary.

Reaction with Phenylmagnesium Bromide

To a solution of phenylmagnesium bromide containing 2.5 molecules of magnesium to one molecule of ester, 28 grams of the ester of the stable acid were added. The orange-colored Grignard product was decomposed with iced hydrochloric acid and the solution treated in the usual way. From the oily product left after removal of the ether, two fractions were separated by distillation under diminished pressure; the lower-boiling fraction was identified as the original ester—

9 grams were recovered unchanged. The higher-boiling fraction, distilling at 285°–290° (18 mm.), solidified in contact with alcohol; yield, 25.5 grams. The solid crystallizes from alcohol in fine, white needles melting at 93°.

Analysis:

0.1530 gram substance gave 0.4950 gram CO_2 and 0.0876 gram H_2O.

	Calculated for $C_{29}H_{26}O$	Found
C	88.46	88.23
H	6.41	6.36

The substance is β-phenyl-γ-benzalpropylphenyl ketone, previously obtained by the action of phenylmagnesium bromide on cinnamylidenacetophenone:[1]

$$C_6H_5CH : CHCH : CHCOC_6H_5 + C_6H_5MgBr \longrightarrow C_6H_5CH : CHCH(C_6H_5)CH_2COC_6H_5$$

1,1,3,5-Tetraphenyl-4-pentene-1-ol, $C_6H_5CH : CHCH(C_6H_5)CH_2C(C_6H_5)_2OH$.—Thirteen and one-half grams of solid β-phenyl-γ-benzalpropylphenyl ketone were added slowly to a solution of phenylmagnesium bromide containing 2 molecules of reagent to one molecule of ketone. After allowing the reaction mixture to stand at room temperature for an hour, it was decomposed with iced hydrochloric acid. The solid which appeared at once in the ether layer was separated and washed with ether. A quantitative yield of tertiary alcohol was obtained. It was purified by recrystallization from alcohol, from which it separated in fine, white needles melting at 134°. The substance is very soluble in acetone, chloroform and benzene, less soluble in ether, methyl and ethyl alcohols.

Analysis:

0.1858 gram substance gave 0.6078 gram CO_2 and 0.1093 gram H_2O.

	Calculated for $C_{29}H_{26}O$	Found
C	89.23	89.21
H	6.66	6.53

[1] Kohler: Ber. d. chem. Ges., **38**, 1204.

The Grignard reaction showed that the substance is a hydroxyl compound. When the solid was added to a solution of ethylmagnesium bromide, evolution of gas took place and on decomposition of the magnesium derivatives, all the original material was recovered unchanged.

Attempts to eliminate one molecule of water from this tertiary alcohol were unsuccessful.

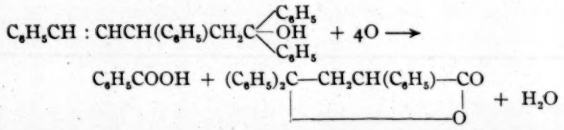
The structure of the tertiary alcohol was established by oxidation. Four grams of the solid were dissolved in acetone and treated with finely powdered potassium permanganate at room temperature. The mixture was allowed to stand overnight and the excess of permanganate was then decolorized with an acetone solution of sulphur dioxide. The oxides of manganese were separated by filtering with suction and washed with hot acetone. The acetone solution deposited a crystalline solid, which was carefully washed with cold alcohol and purified by recrystallization from the same solvent. It separated in long, iridescent needles melting at 157°; 1.5 grams were obtained from this solution.

Analysis:

0.1549 gram substance gave 0.4752 gram CO_2 and 0.0800 gram H_2O.

	Calculated for $C_{22}H_{18}O_2$	Found
C	84.07	83.66
H	5.73	5.73

Subsequent extraction of the oxides of manganese with hot water gave a solution from which one gram of benzoic acid was separated. The oxides of manganese were finally dissolved in sulphuric acid to which sulphur dioxide was added, and the solution extracted with ether. On evaporation of the ether 0.6 gram of the same solid that separated from the acetone solution was obtained. Analysis and reactions showed that this substance is the lactone of γ-hydroxytriphenylbutyric acid, formed by loss of one molecule of water from the γ-hydroxy acid which is a primary product of oxidation.



The lactone is very soluble in acetone, chloroform and benzene, much less soluble in ether, methyl and ethyl alcohol. It does not dissolve in sodium carbonate and dissolves readily in potassium hydroxide. The lactone is precipitated unchanged from its solution in potassium hydroxide, even when the reaction is carried out in a freezing mixture.

With a view of determining whether the isomeric methyl esters of cinnamylidenacetic acid show a difference in their action with organic magnesium compounds, reactions with the two esters and phenylmagnesium bromide were carried out at the same time under conditions as nearly alike as possible. A much larger excess of Grignard reagent was prepared than in the previous reaction with phenylmagnesium bromide, 4 molecules of reagent to one molecule of ester being used. There was no apparent difference in the action of the two esters, both magnesium derivatives soon acquiring a bright, orange color. The Grignard products were decomposed and treated in the usual way. As the ether extract from the two solutions evaporated, both deposited crystals of the same ketone, β-phenyl-γ-benzalpropylphenyl ketone. The product from the reaction with the ester of the allo acid, however, crystallized with greater ease and gave a much larger crop of ketone crystals. From 10 grams of this ester 10 grams of ketone were obtained—a 60 per cent. yield; no other product could be isolated.

Portions of the products from the two reactions were saponified with alcoholic potassium hydroxide. No acid was found in the solution obtained from the product of the reaction with the ester of the allo acid. An acid, however, was isolated from the other solution. Accordingly, the whole of the product from the reaction with the ester of the stable acid was

saponified and stable cinnamylidenacetic acid, equivalent to one-third of the ester used, was separated. No trace of any other acid could be found. From the 6 grams of the ester of the stable acid that had reacted, 7.5 grams of β-phenyl-γ-benzalpropylphenyl ketone were obtained—a 75 per cent. yield.

Reaction with Benzylmagnesium Bromide

An ether solution of 14 grams of the ester of the stable acid was allowed to react with a solution of benzylmagnesium bromide in the same solvent. After a few grams of the ester had been added, the magnesium mixture assumed a dark green color, and finally when 14 grams had been added an oil began to separate from the ether. When this first appeared the reaction was stopped and the Grignard product was decomposed at once with iced hydrochloric acid; the solution was extracted and the ether extract washed and dried in the usual way. The liquid left after evaporation of the ether was treated with alcoholic potassium hydroxide, and after allowing the mixture to stand overnight, the alcohol was distilled off and the residue treated with water.

The portion of the product insoluble in water was extracted with ether, the ethereal solution washed and dried over calcium chloride, and after removal of the solvent the yellow liquid was fractioned under diminished pressure; 2 grams of a very mobile, lemon-yellow liquid distilled at 200° (10 mm.) and 12.5 grams of a viscous, lemon-yellow liquid distilled at 265 (15 mm.). There were several grams of residue left in the Claisen flask. The higher boiling fraction is β-benzyl-γ-benzalpropylbenzyl ketone,

$$C_6H_5CH : CHCH(CH_2C_6H_5)CH_2COCH_2C_6H_5$$

Analysis:

0.1566 gram substance gave 0.5071 gram CO_2 and 0.0969 gram H_2O.

	Calculated for $C_{30}H_{24}O$	Found
C	88.23	88.31
H	7.06	6.87

Dibrom-β-benzyl-γ-benzalpropylbenzyl Ketone, $C_6H_5CHBrCHBrCH(CH_2C_6H_4)CH_2COCH_2C_6H_5$.—Two grams of the ketone were dissolved in carbon bisulphide and the solution cooled in a freezing mixture and treated with a solution of bromine in the same solvent. The calculated quantity of bromine was instantly decolorized. Evaporation of the solvent in a current of air deposited a white solid, which was purified by recrystallization from a mixture of ligroin and chloroform. It melts at 165°.5 and is very soluble in acetone and chloroform, not so soluble in ether, ligroin and ethyl alcohol.

Analysis:

0.1393 gram substance gave 0.3063 gram CO_2 and 0.0608 gram H_2O.

	Calculated for $C_{30}H_{24}OBr_2$	Found
C	60.00	59.96
H	4.80	4.84

Sufficient material was accumulated for purification of the lower-boiling fraction. This was α,α-dibenzyl-δ-benzalcrotonyl alcohol,

$$C_6H_5CH : CHCH : CHC(CH_2C_6H_5)_2OH$$

Analysis:

0.1496 gram substance gave 0.4826 gram CO_2 and 0.0932 gram H_2O.

	Calculated for $C_{30}H_{28}O$	Found
C	88.23	87.98
H	7.06	6.92

The Grignard reaction showed that the substance is a hydroxyl compound. There was a steady evolution of gas when the liquid was treated with ethylmagnesium bromide.

Tetrabrom-α,α-dibenzyl-δ-benzalcrotonyl Alcohol, $C_6H_5CHBrCHBrCHBrCHBrC(CH_2C_6H_5)_2OH$.—Two grams of tertiary alcohol were dissolved in chloroform and treated with a chloroform solution of bromine as long as instantaneous decolorization took place. As the solvent evaporated, fine

needles appeared, which were filtered and washed with hot methyl alcohol. The product thus treated melts at 227° with evolution of gas and charring. It was impossible to purify it further by recrystallization, for the melting point of the solid was lowered ten degrees by one recrystallization from a mixture of cold chloroform and methyl alcohol. The carefully washed solid was therefore used for analyses. It is very soluble in acetone, chloroform and ethyl alcohol, less soluble in ether and ligroin.

Analysis:

I. 0.1613 gram substance gave 0.2772 gram CO_2 and 0.0538 gram H_2O.

II. 0.1538 gram substance gave 0.2630 gram CO_2 and 0.0519 gram H_2O.

	Calculated for $C_{25}H_{24}OBr_4$	Found	
		I	II
C	45.45	46.86	46.63
H	3.63	3.70	3.74

β-Benzyl-γ-benzalbutyric Acid,

$C_6H_5CH : CHCH(CH_2C_6H_5)CH_2COOH$. — On acidifying the aqueous solution obtained after saponification of the original product with alcoholic potassium hydroxide, 1.2 grams of an oily acid separated which solidified at once in contact with alcohol. It was recrystallized from a mixture of acetone and ligroin, from which it separated in heavy, iridescent plates melting at 144°.

Analysis:

0.1500 gram substance gave 0.4447 gram CO_2 and 0.0910 gram H_2O.

	Calculated for $C_{18}H_{18}O_2$	Found
C	81.20	80.85
H	6.76	6.74

The acid is very soluble in acetone, methyl and ethyl alcohol, not so soluble in ligroin and chloroform.

Molecular weight determined in boiling acetone ($K = 1710$).

Solvent Grams	Substance Gram	Elevation of boiling point	Molecular weight
41.8	0.1198	0.019	258
	0.4605	0.071	265
	0.7219	0.109	271
	0.9874	0.151	267
		Average	265
		Calculated for $C_{18}H_{18}O_2$	266

The acid was dissolved in a solution of sodium carbonate and oxidized with potassium permanganate; benzoic acid and benzylsuccinic acid were the oxidation products isolated. The benzylsuccinic acid was identified by comparison with a specimen on hand. The reaction, represented by the following equation, establishes the structure of the substance:

$$C_6H_5CH : CHCH(CH_2C_6H_5)CH_2COOH + 4O = C_6H_5COOH + C_6H_5CH_2CH(COOH)CH_2COOH$$

Methyl β-Benzyl-γ-benzalbutyrate, $C_6H_5CH : CHCH(CH_2C_6H_5)CH_2COOCH_3$.—The ester was prepared by treating the acid with a saturated solution of hydrochloric acid in methyl alcohol. After allowing the mixture to stand overnight, it was poured upon iced sodium carbonate and the solution extracted with ether. The solid which separated on evaporation of the ether was purified by recrystallization from methyl alcohol. It melts at 66°.

Analysis:

0.1554 gram substance gave 0.4640 gram CO_2 and 0.0984 gram H_2O.

	Calculated for $C_{19}H_{20}O_2$	Found
C	81.42	81.43
H	7.14	7.03

Reaction with Ethylmagnesium Bromide

An ethereal solution of 10 grams of the ester of the stable acid was added very slowly to an ethereal solution of ethylmagnesium bromide containing 4 molecules of magnesium to one molecule of ester. A very vigorous reaction took place even at —10° and the magnesium mixture soon acquired a

brilliant green color, indicating the formation of secondary products. When all the ester had reacted, the Grignard product was decomposed with iced hydrochloric acid, the solution extracted with ether, the ether extract washed with sodium carbonate and dried over calcium chloride. On evaporation of the solvent a yellow liquid was obtained. This was treated with alcoholic potassium hydroxide and after allowing the mixture to stand several hours, the alcohol was distilled off and the residue treated with water. The portion insoluble in water was extracted with ether and the ethereal extract washed and dried. After removal of the solvent the liquid was distilled under reduced pressure. One gram of pale yellow liquid distilled at 169° (10 mm.), leaving several grams of dark residue in the Claisen flask.

On acidifying the aqueous solution, 3.5 grams of acid separated; it was purified by recrystallization from a mixture of acetone and ligroin, from which it separated in fine, colorless needles melting at 179°. Analyses indicated that it was a secondary product.

As the treatment with potassium hydroxide might have been too vigorous, the reaction was repeated and the product was not saponified but was at once distilled under diminished pressure. Two fractions were separated; the lower-boiling one was a pale yellow, mobile liquid distilling at 169° (10 mm.). It is α,α-diethyl-δ-benzalcrotonyl alcohol, formed by replacement of the methoxyl group of the ester and subsequent 1,2-addition of a second molecule of ethylmagnesium bromide to the unsaturated ketone thus formed.

$$C_6H_5CH : CHCH : CHCOOCH_3 + C_2H_5MgBr \longrightarrow [C_6H_5CH : CHCH : CHCOC_2H_5]$$

$$[C_6H_5CH : CHCH : CHCOC_2H_5] + C_2H_5MgBr \longrightarrow C_6H_5CH : CHCH : CHC(C_2H_5)_2OH$$

Analysis:

0.1634 gram substance gave 0.4979 gram CO_2 and 0.1324 gram H_2O.

	Calculated for $C_{15}H_{20}O$	Found
C	83.33	83.10
H	9.25	9.00

The liquid was shown to be a hydroxyl compound by treatment with ethylmagnesium bromide. There was a steady evolution of gas and on decomposition of the magnesium derivative the original material was entirely recovered.

Several attempts were made to eliminate one molecule of water from this tertiary alcohol. Ten grams of the liquid were heated with 3 molecules of acetic anhydride for three hours over a free flame. The tertiary alcohol was recovered unchanged from the solution. No reaction, moreover, took place when the liquid was heated for four hours at 215° in a sealed tube with excess of acetic anhydride, and attempts to split off water by the use of oxalic acid were likewise unsuccessful.

The higher-boiling fraction, separated by distillation under diminished pressure, was a heavy, viscous, yellow liquid boiling at 278°–285° (10 mm.). After standing overnight the liquid deposited fine, white needles melting at 136°. The solid was purified by recrystallization from ethyl alcohol, after carefully washing it free from the yellow liquid with ether. Analyses indicated that this solid is also a secondary product; it is an ester, from which, by saponification with potassium hydroxide, an acid melting at 230° was obtained. It was not studied further and its structure was not established. The higher-boiling fraction is doubtless a mixture of secondary products, which would be anticipated in the Grignard reaction with methyl cinnamylidenacetate.[1]

In the reaction between this ester and ethylmagnesium bromide, the proportion of α,α-diethyl-δ-benzalcrotonyl alcohol and the higher-boiling products is dependent upon the conditions under which the reaction is allowed to take place. If the magnesium mixture is kept at —10° and the ester is added very slowly, a 50–55 per cent. yield of the tertiary alcohol may be separated and a comparatively small yield of secondary products. If, however, the temperature of the reaction mixture is allowed to rise a much larger proportion of secondary products is obtained.

CHEMICAL LABORATORY
BARNARD COLLEGE
May, 1911

[1] Kohler: THIS JOURNAL, **34**, 568.

REVIEWS.

TRATTATO DI CHIMICA INORGANICA GENERALE E APPLICATA ALL' INDUSTRIA. DOTT. ETTORE MOLINARI, Professore di Chimica industriale alla Società d'Incoraggiamento d' Arti e Mestieri e di merceologia all'Università Commerciale Luigi Bocconi in Milano. 280 Incisioni nel Testo, 1 Tavola in Cromolitografia e 2 Tavole in Fototipia. Terza edizione riveduta e ampliata. Milano: Ulrico Hoepli. 1911. pp. xvii + 923. Price, L. 16.

To this, the first volume of a work, of which the second volume dealing with organic chemistry was reviewed last year,[1] the same unqualified praise is due for the surprising amount of useful information and sound science compressed into a limited space. Thus, for example, under "air," in thirty-two pages, is given a comprehensive account of liquid-air machines and their practical operation, with data as to cost, power required, and efficiency, etc., Linde's, Claude's and Pictet's systems, fractionation of the liquid and utilization of the oxygen and nitrogen, methods of fixing the latter as practiced in Norway, America, Switzerland, Germany, Italy, France and England, with a summary of recent inventions and patents, action of calcium cyanamide as a fertilizer, besides records of atmospheric pressure and a brief account of the properties of the rare gases. Commercial objects and practical requirements are kept constantly in view; current prices and localities and quantity of production are quoted throughout, and the information is brought down to about 1910. There are numerous clear illustrations of apparatus and an index. For the chemist who is interested in practical applications the book can be highly recommended.

B. B. TURNER.

AN INTRODUCTION TO THERMODYNAMICS FOR ENGINEERING STUDENTS. BY JOHN MILLS. Ginn & Co. pp. 136. Price, $2.00.

In studying any subject with a mathematical basis two phases of the mental process involved may be distinguished, as distinct as the ability to read and speak a foreign language. To comprehend the fundamental principles, when their demonstration is presented, and the power to reproduce that demonstration is rightly placed first; experience shows, however, that real mastery of the subject is only reached when the student can readily apply those principles to concrete instances, with definite data. This is peculiarly the case with such an abstruse subject as thermodynamics, and its applications to chemical problems, so that while the above-named book, as its title implies, deals solely with questions of interest to

[1] THIS JOURNAL, 44, 202.

engineers, expansion of gases, properties of steam and water flow of gases, etc., it would greatly advantage most students of physical chemistry to work through a number of the simple problems with which the book abounds. The text is usually well written and the explanations clear, while many tables and diagrams give the facts a reality and readily intelligible appearance. The use of Fahrenheit temperatures, British thermal units, foot pounds, etc., which is justified by the purpose of the book, will only provide a little extra arithmetical exercise for the chemist. The author is to be heartily congratulated on the production of a useful little book.

B. B. TURNER.

INTRODUCTION TO GENERAL CHEMISTRY. BY JOHN TAPPAN STODDARD, PH.D., Professor of Chemistry in Smith College. New York: The Macmillan Company. 1910. pp. xviii + 432. Price, $1.60.

The first agreeable thing about this new text is the size of the volume. It contains little more than one-half the number of words contained in similar texts. And yet, the subject matter enclosed by its covers is sufficient with a good teacher to keep a college class very busy for a year. Of course one is curious to know how the author can have accomplished his purpose within such limits. It is stated that the book "is designed as an introduction to advanced study, providing a foundation which shall be both broad and thorough." Although we might expect from such a program a crowding of the page, ease and dignity seem to stamp the work. All the essentials are introduced and yet there is plenty of room. In explanation of how this is possible and how the high purpose of the author has been successfully carried out, we note first that great importance is attached to all those generalizations which, after taking root in the history of the science, have surrounded themselves with a hedge of succinct and very convenient phraseology. Then, when the newer and less universally accepted theories, physical or mathematical, are introduced, they are presented simply, with no defense, and with the chemical bearing exclusively emphasized. The size of the book is affected somewhat by the omission of all pictures. The author is strongly of the opinion that illustrations are unnecessary and at times misleading and he has bravely decided to omit them all.

As reflecting the attitude of the teacher, we read in the preface: "Above all, I have tried to help the student to enter into the spirit of chemistry and to acquire the scientific point of view." One path towards this purpose is by free use of the quantitative method; and there are many references in

the text to Stoddard's own little book of quantitative experiments for beginners which was reviewed in THIS JOURNAL.[1] Thus the important laws of chemical combination are presented from the student's experimental results and the quantitative relations are emphasized; but not without the data for illustration. Dr. Minot has just said at Minneapolis, and well said: "Mathematics cannot give any comprehensive expression of complex relations . . . . . For our accuracy it is necessary often to have a number of data presented to our consciousness at the same time." So, for the student's assimilation to proceed with an accuracy of which mathematics is incapable, the statement of the quantitative law must always be accompanied by the illustrative data.

Again, the plan and spirit of the book are reflected by the statement: "So far as is possible, the progress is from the familiar to the unfamiliar, from the known to the unknown." This has been a guiding thought with the author and has strongly regulated the choice of material and the order of its presentation. The advantage of following the periodic system is considered minor to that of proceeding from the familiar and important. This gives an arrangement somewhat unfamiliar to the older chemist. Sulphuric acid is made the basis for the study of all acids and is introduced very early; and in general the substance, element or compound which is most important is for that reason presented first.

The language is clear, and it is convincing because it is simple. A few errors exist, but only such as may be easily corrected in the future editions. The mechanical construction of the book is Macmillan's best. A. J. H.

A LABORATORY MANUAL OF INORGANIC CHEMISTRY. BY EUGENE C. BINGHAM, PH.D. (Johns Hopkins), Professor of Chemistry, Richmond College, Richmond, Virginia, and GEORGE F. WHITE, PH.D. (Johns Hopkins), Associate Professor of Chemistry, Richmond College, Richmond, Virginia. New York: John Wiley & Sons; London: Chapman and Hall, Ltd. 1911. pp. viii + 147. Price, $1.00.

The first section of the book is called "Inorganic Preparations," but comprises nothing more than the laboratory work on nonmetals usually included in the first year's work in chemistry. The second section, called "Qualitative Analysis," is a combination of the study of reactions of the single metals with a scheme of systematic qualitative analysis, closing with the analytical detection of acids. The third section is a brief exposition of principles of quantitative analysis. The authors say in the preface: "The Principles of Physical Chemistry

[1] Vol. 42, 373.

have been freely introduced whenever they seemed necessary to the understanding of the subject at hand, but with as little technical language as possible."

The tendency of the day is to introduce more or less physical chemistry into class and laboratory work in the second college year, and this tendency meets with general approval. Whether it is advisable in the first year seems questionable. The authors have employed these methods sparingly and in a very simple way; yet whether, for example, the help to the student in balancing equations (pages 66–69) by graphic representation of the change in electric charge, will balance the confusion caused in the beginner's mind by such formulas as $P^{3}Cl_{3}^{-1} + Cl_{2}^{\circ} = P^{5}Cl_{5}^{-1}$ or $H_{2}S^{-2} + HN^{5}O_{3} \longrightarrow H_{2}S^{6}O_{4} + N^{2}O + H_{2}O$ (in which the lower figures denote the number of atoms in the molecule, the upper figures and symbols the number and sign of the charges) seems again questionable.

This criticism may not be valid, and if it is valid it applies to only a small part of this book, which as a whole is clear, logical, well written and gives an excellent course of study, although the authors acknowledge that it is not feasible to complete the work outlined in one college year. E. R.

CHEMISTRY FOR BEGINNERS. I. INORGANIC. BY EDWARD HART, PH.D., Professor of Chemistry, Lafayette College, Easton, Pa. Fifth Edition, Revised and Enlarged, with 78 Illustrations and 2 Plates. Easton, Pa.: The Chemical Publishing Co. 1910. pp. viii + 214.

Professor Hart says in the preface: "I have tried to bear constantly in mind that the large majority of those studying chemistry are not likely to become professional chemists, and have therefore taken pains to enlarge upon those topics which all educated persons should understand, such as water purification, fertilizers, the concentration of ores, the roasting of ores, assaying, the iron blast furnace, steel manufacture, etc." A perusal of the volume leads to the belief that the author has performed his task successfully. E. R.

A COURSE IN QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES, with Explanatory Notes. BY OLIN FREEMAN TOWER, PH.D., Hurlbut Professor of Chemistry in Adelbert College of Western Reserve University. Second Edition, Revised. Philadelphia: P. Blakiston's Son & Co. 1911. pp. xiii + 84.

A favorable review of the first edition of this book has already appeared.[1] Evidently the book has been well received by the public as a second edition is so soon printed. E. R.

[1] THIS JOURNAL, 45, 414.

Dizionario di Merceologia e di Chimica Applicata alla conoscenza dei prodotti delle cave e miniere, del suolo e dell'industria, con speciale riguardo ai prodotti alimentari, chimici e farmaceutici. Pel Prof. Dott. Vittorio Villavecchia, Direttore dei laboratori chimici delle Gabelle, con la collaborazione dei Dott. Guido Fabris, Dott. Guido Rossi, Dott. Arnaldo Bianchi. Terza edizione, completamente riveduta, corretta ed ampliata. Vol. I, Lettere A-M. Milano: Ulrico Hoepli. 1911. pp. xiv + 779. Price, L. 15.

For purposes of reference and as a supplement to other sources of information, this alphabetical list of commercial substances should be very useful. The large number of separate headings (this volume appears to contain about 2000) makes possible the inclusion of most raw materials, textiles, pharmaceutical substances, drugs, foodstuffs, metals and minerals, dyes, etc., and short articles on such varying topics as dentifrices and densimetry, weights and measures and jujubes. The English, French, German and Spanish equivalents are given for each substance, together with many facts of interest for their practical and commercial bearing. Thus, under Menthol, a typical article, in about 600 words we are told its properties and tests, uses, derivatives (with their trade names), production in kilograms, price, and the (Italian) tariff. Indigo receives 10 columns (about 4,000 words), including a short account of its synthesis; Cement receives 8 columns; and Cotton twelve. Emphasis is placed on commercial qualities and brands, but purely chemical information is necessarily restricted. The second volume is promised shortly.

B. B. Turner.

A Short Hand-Book of Oil Analysis. By Augustus H. Gill, S.B., Ph.D., Professor of Technical Analysis at the Massachusetts Institute of Technology, Boston, Mass. Sixth edition, revised and enlarged. Philadelphia and London: J. B. Lippincott & Co. 1911. pp. 188.

The sixth edition of Gill's "Oil Analysis," recently issued, following soon after the preceding edition, indicates a brisk demand in the field of analysis that this book occupies.

Some additional tests appear in this edition in the line of the expansive use of mineral oils and vegetable oils that have recently come into the trade, notably the carbon test for auto oils and the gasoline test. More space is given to greases and miscellaneous oils, such as transformer and turbine lubricants and reduced oils. Acheson's oildag is mentioned. Some changes in the tables and useful additions, especially the formulas to change the readings of one viscosimeter to another, are noted. This book is indispensable in the field it covers.

C. F. Mabery.